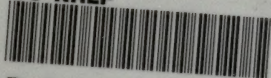
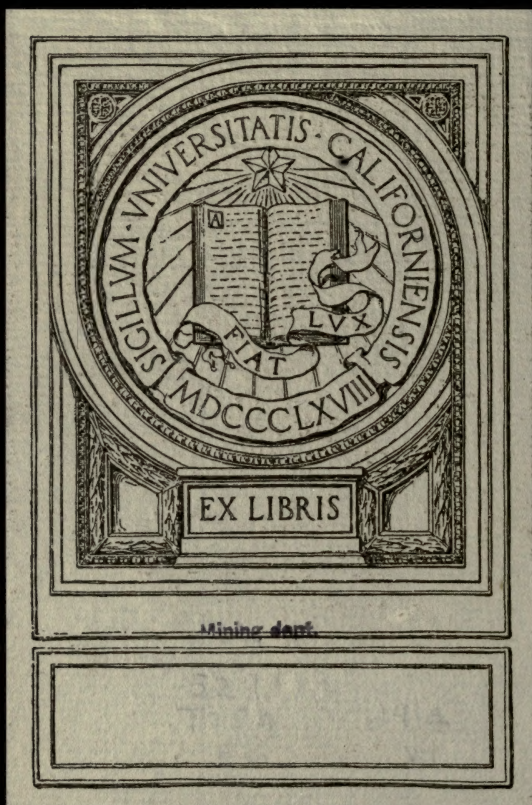


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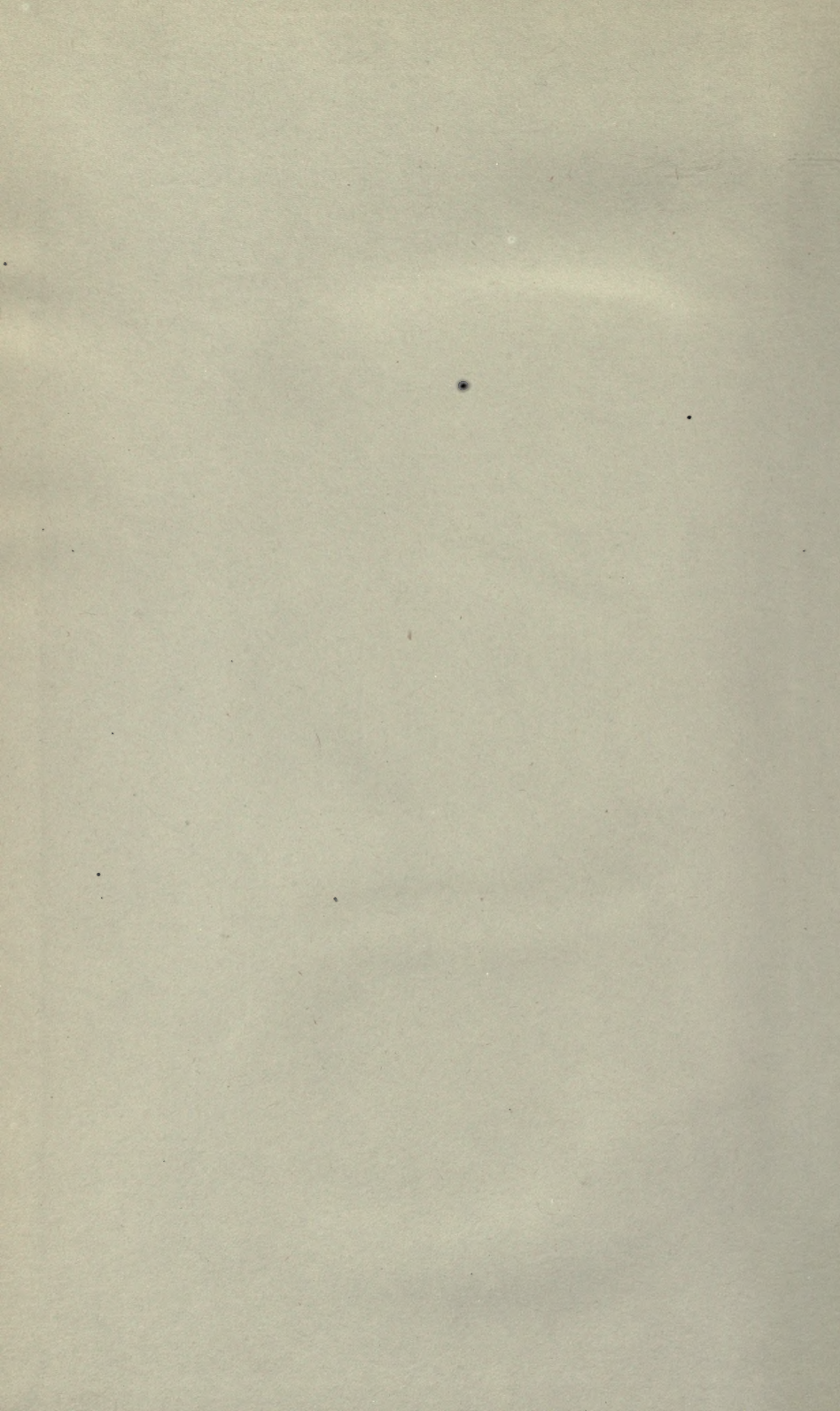


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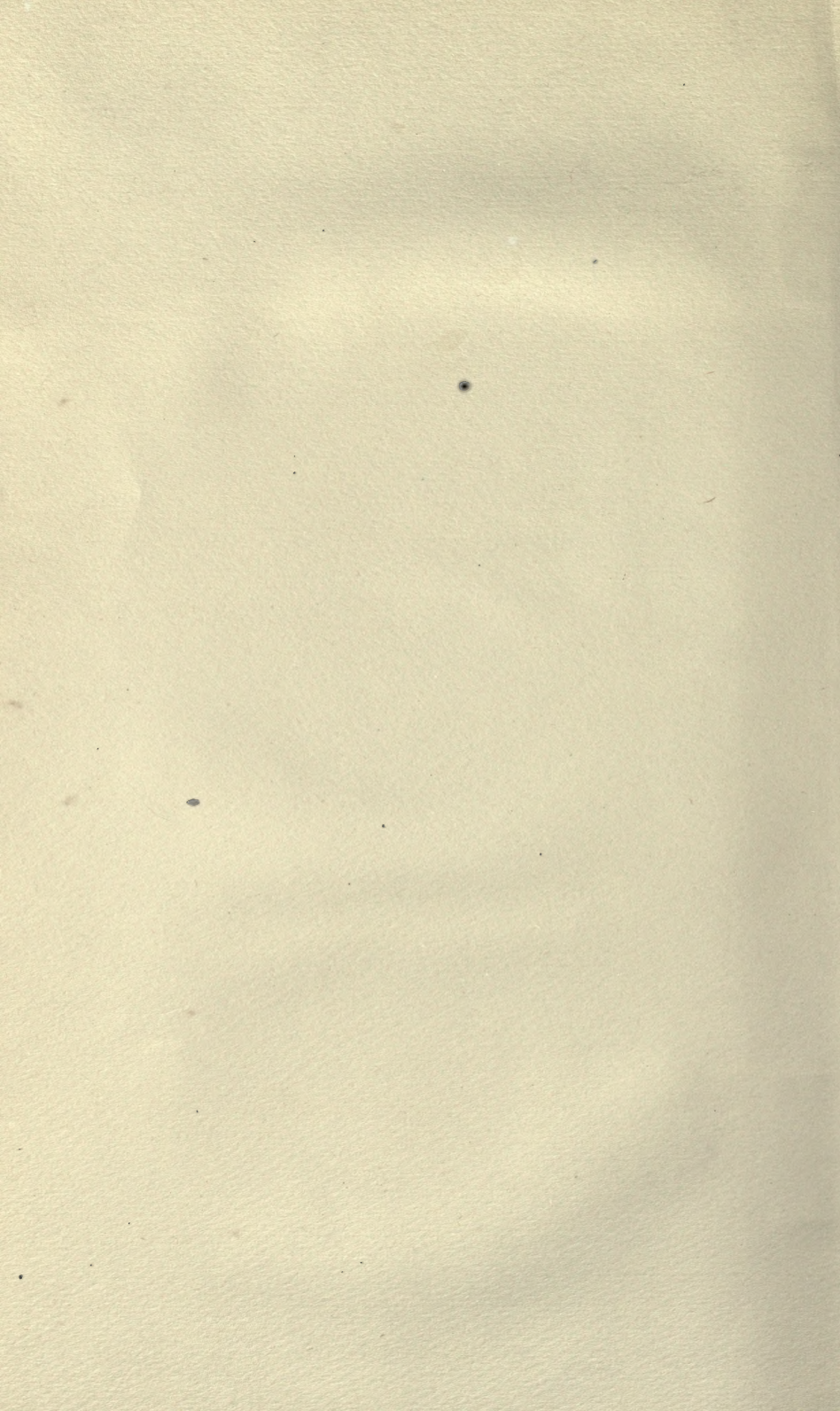
















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WILLIAM T. HALL**

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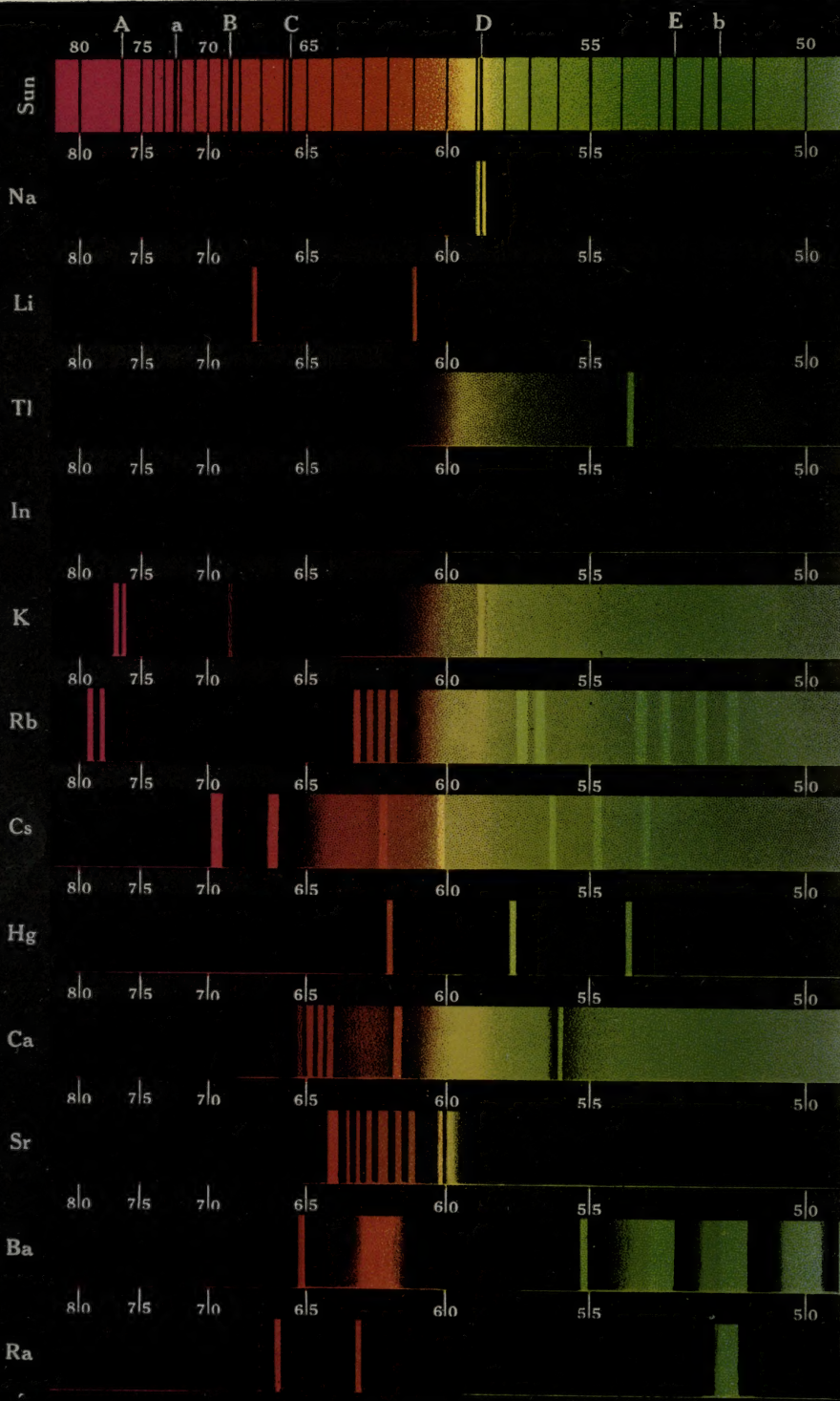
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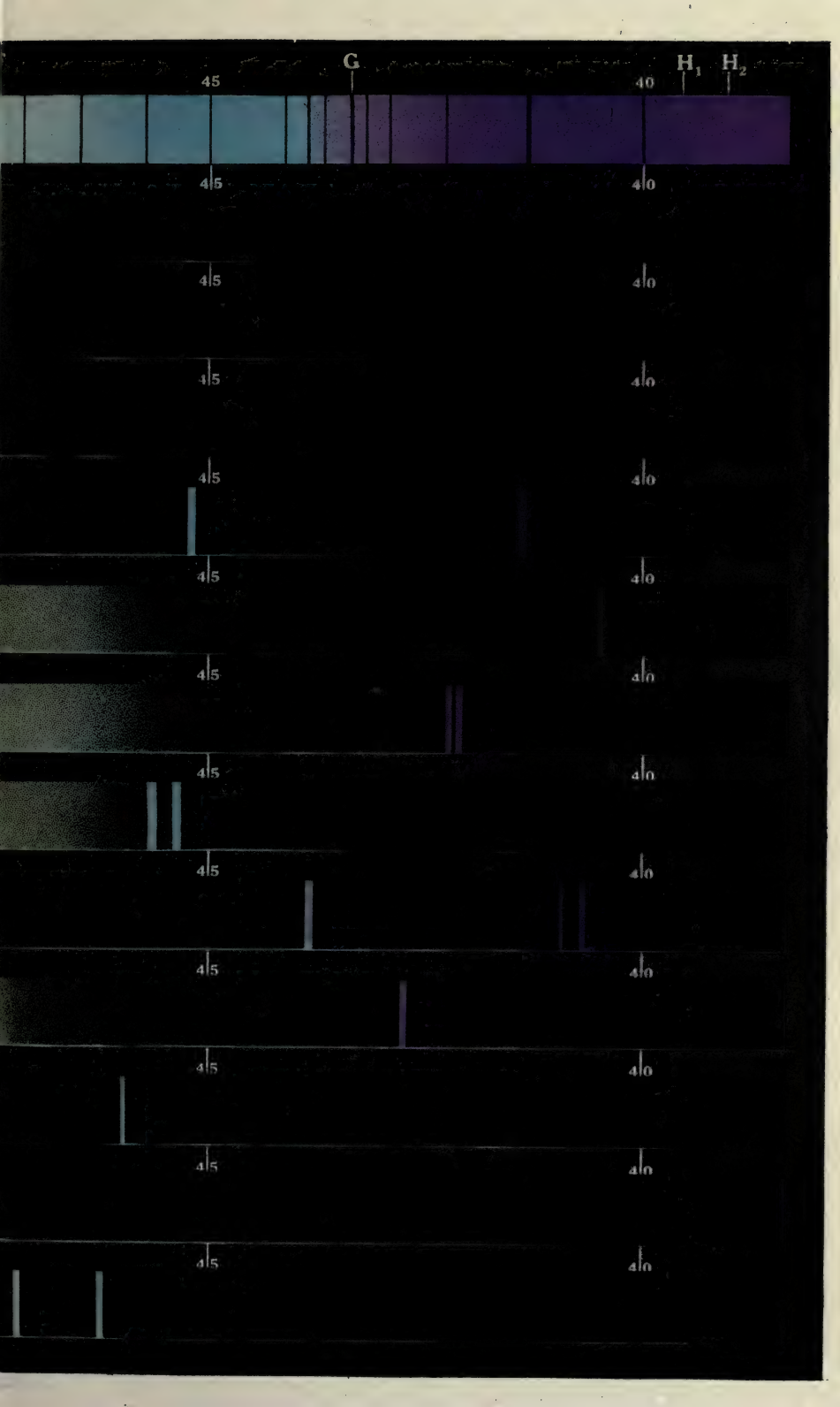
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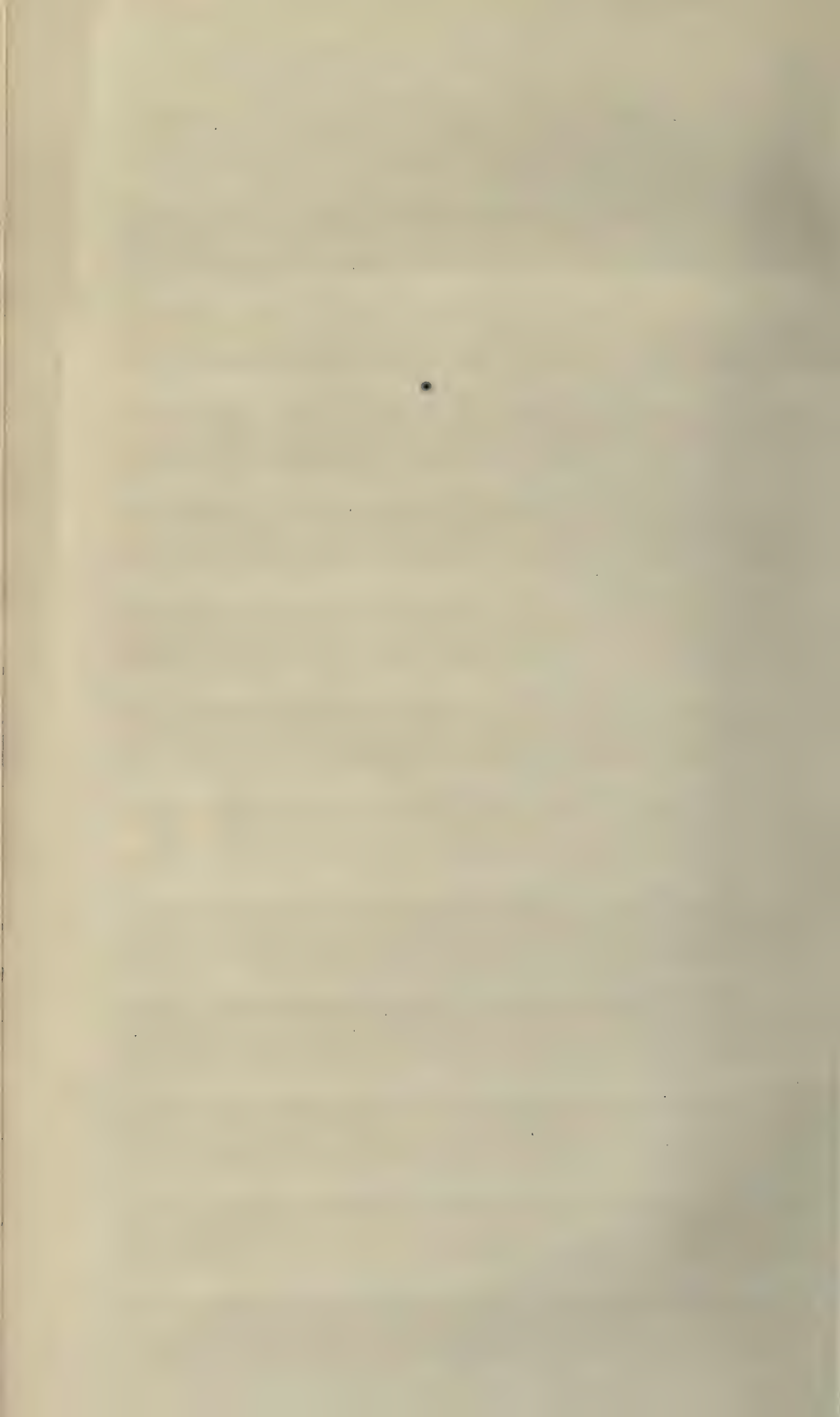












# ANALYTICAL CHEMISTRY.

BY

F. P. TREADWELL, PH.D.,

*Professor of Analytical Chemistry at the Polytechnic Institute of Zürich.*

AUTHORIZED TRANSLATION

BY

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*Assistant Professor of Analytical Chemistry, Massachusetts Institute of Technology.*

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## PREFACE TO THE FIRST EDITION.

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HAVING been repeatedly requested by former pupils to publish the lectures on Analytical Chemistry given by me at this Institute since 1882, and not having time then to do it myself, I permitted the "Verein der Polytechniker" in 1885 to print in manuscript form the notes of one of my students.

This output met with such a friendly reception that in 1888 a second edition became necessary. Subsequently I decided to publish the material in book form, with a radical rearrangement; so that this text-book of Analytical Chemistry represents a somewhat amplified repetition of my lectures.

This little book is intended not only for laboratory use, but also for self-study. With each element the mineralogical occurrence, crystalline form, and isomorphous relations are briefly mentioned. Then, after explaining the reactions, I give the methods of separation in the form of tables; because, contrary to the views of many, I have in this way obtained the best results in teaching. These tables are summarized charts with which the student can quickly find his bearings.

Much weight will be placed upon the determination of the sensitiveness of the single reactions, as is explained on page 43, because the beginner becomes in this way at once familiar with the solubility of the most important salts, and also with simple stoichiometrical calculations. Thus the approximate solubility of potassium chloroplatinate, for example, is found from the following determination of the sensitiveness of the reaction by which it is formed:

If 100 cc. of the solution contain 0.156 gm. potassium, one finds that the formation of the chloroplatinate, at ordinary temperatures, only takes place on addition of a little alcohol; but on in-

iii



creasing slightly the amount of potassium in the solution, it takes place immediately. We can, therefore, assume that the solution, which contains 0.156 gm. of potassium per 100 c.c. water, is saturated with chloroplatinate; hence the amount of the latter may be calculated:

$$\begin{aligned} K_2 : K_2PtCl_6 &= 0.156 : x; \\ 78.3 : 485.8 &= 0.156 : x; \\ x &= 0.97. \end{aligned}$$

The result shows that 100 c.c. of water, at ordinary temperatures, dissolve 0.97 gm. of  $K_2PtCl_6$ , while accurate determinations at 20° C. have given the value 1.12. The difference, about 12 per cent., is explained by the facts that we did not work at exactly 20° C., nor with absolutely pure water; the solution also contains an excess of chloroplatinic acid, whereby the solubility of the potassium chloroplatinate is diminished; but at the same time the values obtained in this way permit a very good comparison of the solubilities of the different salts. From the sensitiveness of the reaction between a potassium salt and tartaric acid, the solubility of the potassium acid tartrate may be found to be 0.38; so that the solubility of the potassium chloroplatinate is to that of the potassium acid tartrate as 0.97 : 0.38; the potassium tartrate is about three times as insoluble as the chloroplatinate, etc.

The size of the book does not permit going into the microchemical detection of the different elements. We have, however, in the excellent work of H. Behrens, "Anleitung zur mikrochemischen Analyse," a reference book of the highest rank.

In publishing this, the first volume of the work, I beg of my colleagues and fellow chemists to kindly inform me of any errors or omissions.

F. P. TREADWELL.

ZURICH, April 29, 1899.

## TRANSLATOR'S NOTE.

---

THE translator wishes to express his sincere thanks to Professor Treadwell for his kindness and good wishes with regard to the preparation of this translation, to Professor A. A. Noyes, Professor Henry Fay, and Mr. H. S. Walker of the Massachusetts Institute of Technology, for their advice and criticism of the proof, and especially to Dr. W. O. Holway of Newton Centre for his many valuable suggestions.

In preparing the third edition, the text has been carefully revised and a number of important changes made. A new chart of the more important spectra is given, and the wave lengths of the different rays of light stated. Oxidation and reduction equations are explained more on the basis of the electron conception of valence than in accordance with the old dualistic theory, and in this, as well as in other points, the translation does not follow the German text.





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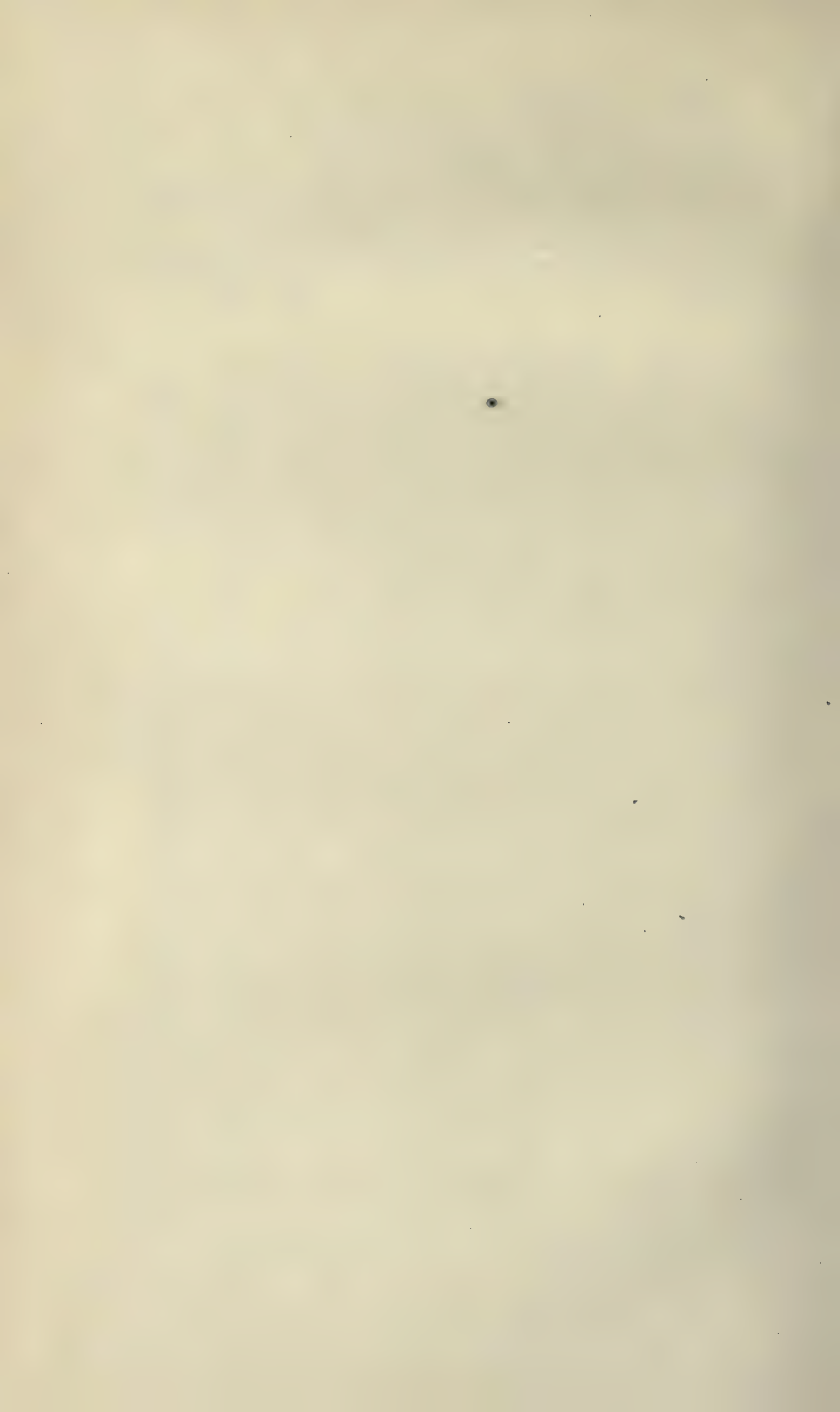
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	Sym- bol.	Atomic Weight.		Sym- bol.	Atomic Weight.
Aluminium . . . . .	Al	27.1	Molybdenum . . . . .	Mo	96.0
Antimony . . . . .	Sb	120.2	Neodymium . . . . .	Nd	144.3
Argon . . . . .	A	39.88	Neon . . . . .	Ne	20.2
Arsenic . . . . .	As	74.96	Nickel . . . . .	Ni	58.68
Barium . . . . .	Ba	137.37	Nitron ( <sup>radium</sup> emanation) . . . . .	Nt	222.4
Bismuth . . . . .	Bi	208.0	Nitrogen . . . . .	N	14.01
Boron . . . . .	B	11.0	Osmium . . . . .	Os	190.9
Bromine . . . . .	Br	79.92	Oxygen . . . . .	O	16.00
Cadmium . . . . .	Cd	112.40	Palladium . . . . .	Pd	106.7
Cæsium . . . . .	Cs	132.81	Phosphorus . . . . .	P	31.04
Calcium . . . . .	Ca	40.07	Platinum . . . . .	Pt	195.2
Carbon . . . . .	C	12.00	Potassium . . . . .	K	39.10
Cerium . . . . .	Ce	140.25	Praseodymium . . . . .	Pr	140.6
Chlorine . . . . .	Cl	35.46	Radium . . . . .	Ra	226.4
Chromium . . . . .	Cr	52.0	Rhodium . . . . .	Rh	102.9
Cobalt . . . . .	Co	58.97	Rubidium . . . . .	Rb	85.45
* Columbium . . . . .	Cb	93.5	Ruthenium . . . . .	Ru	101.7
Copper . . . . .	Cu	63.57	Samarium . . . . .	Sa	150.4
Dysprosium . . . . .	Dy	162.5	Scandium . . . . .	Sc	44.1
Erbium . . . . .	Er	167.7	Selenium . . . . .	Se	79.2
Europium . . . . .	Eu	152.0	Silicon . . . . .	Si	28.3
Fluorine . . . . .	F	19.0	Silver . . . . .	Ag	107.88
Gadolinium . . . . .	Gd	157.3	Sodium . . . . .	Na	23.00
Gallium . . . . .	Ga	69.9	Strontium . . . . .	Sr	87.63
Germanium . . . . .	Ge	72.5	Sulphur . . . . .	S	32.07
† Glucinum . . . . .	Gl	9.1	Tantalum . . . . .	Ta	181.5
Gold . . . . .	Au	197.2	Tellurium . . . . .	Te	127.5
Helium . . . . .	He	3.99	Terbium . . . . .	Tb	159.2
Hydrogen . . . . .	H	1.008	Thallium . . . . .	Tl	204.0
Indium . . . . .	In	114.8	Thorium . . . . .	Th	232.4
Iodine . . . . .	I	126.92	Thulium . . . . .	Tm	168.5
Iridium . . . . .	Ir	193.1	Tin . . . . .	Sn	119.0
Iron . . . . .	Fe	55.84	Titanium . . . . .	Ti	48.1
Krypton . . . . .	Kr	82.92	Tungsten . . . . .	W	184.0
Lanthanum . . . . .	La	139.0	Uranium . . . . .	U	238.5
Lead . . . . .	Pb	207.10	Vanadium . . . . .	V	51.0
Lithium . . . . .	Li	6.94	Xenon . . . . .	Xe	130.2
Lutecium . . . . .	Lu	174.0	Ytterbium (Neoytterbium) . . . . .	Yb	172.0
Magnesium . . . . .	Mg	24.32	Yttrium . . . . .	Yt	89.0
Manganese . . . . .	Mn	54.93	Zinc . . . . .	Zn	65.37
Mercury . . . . .	Hg	200.6	Zirconium . . . . .	Zr	90.6

\* Also called *niobium*, Nb.

† Also called *beryllium*, Be.



# QUALITATIVE ANALYSIS.

---

## GENERAL PRINCIPLES.

By Chemical Analysis is understood all those operations which are performed in order to determine the constituents of a chemical compound (or a mixture of chemical compounds). Chemical Analysis is subdivided into Qualitative Analysis and Quantitative Analysis.

Qualitative Analysis treats of the methods for determining the nature of the constituents of a substance, while Quantitative Analysis treats of the methods for determining *in what proportion* the constituents are present in any compound or mixture of compounds.

In order to recognize a body we change it, usually with the help of a substance of known nature, into a new compound which possesses distinctive properties. This transformation we call a *chemical reaction*; and the substance by means of which the reaction is brought about, the *reagent*.

We distinguish between reactions in the *wet way* and reactions in the *dry way*.

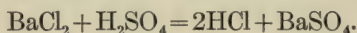
### I. REACTIONS IN THE WET WAY.

For the purpose of qualitative analysis only such reactions are applicable as are easily perceptible to our senses. A reaction is known to take place—

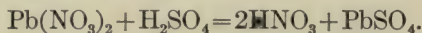
- (a) by the formation of a precipitate;
- (b) by a change of color;
- (c) by the evolution of a gas.



A precipitation always takes place when an insoluble substance is formed by means of a chemical decomposition. If dilute sulphuric acid is added to a solution of a barium salt, a white powdery precipitate of barium sulphate is obtained:



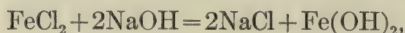
On the other hand, soluble lead salts also give with dilute sulphuric acid a white powdery precipitate:



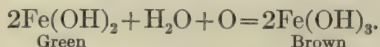
Sulphuric acid, therefore, is a reagent for both barium and lead compounds. But in order to determine whether the precipitate formed is barium sulphate or lead sulphate it must be subjected to a further test, because both substances look alike. If they are heated on charcoal with addition of sodium carbonate, they behave very differently; the lead sulphate is reduced to a metal, and the barium sulphate is only changed to carbonate.

It follows from this example that one must never be content with a single reaction for the detection of a body, but its presence must be verified by a confirmatory test.

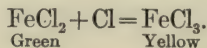
If to a solution of ferrous chloride (obtained by the solution of metallic iron in hydrochloric acid) some sodium hydroxide is added, a greenish-white precipitate of ferrous hydroxide is formed:



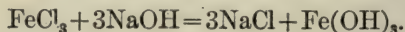
which, on standing in contact with the air, changes to dark green, almost black, and finally becomes brown, the compound having been oxidized by means of atmospheric oxygen to ferric hydroxide:



If chlorine water is added to the green solution of ferrous chloride, a change of color takes place, due to the oxidation of the ferrous salt to a ferric one:



If now sodium hydroxide is added to the yellow solution, the brown precipitate of ferric hydroxide is immediately formed:

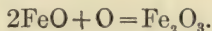


Sodium hydroxide is, therefore, a reagent for ferrous as well as for ferric salts; and although the two precipitates cannot be mistaken for one another, yet, for the sake of certainty, it is advisable that the beginner should make a confirmatory test.

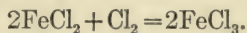
We saw that the green ferrous chloride was changed by means of chlorine water into the yellow ferric salt, and recognized that a reaction had taken place by means of the change in color. Color reactions in the wet way occur very often because of an *oxidation*, as in the case just mentioned; but, conversely, they may take place in consequence of a *reduction*.

We shall constantly have to perform oxidations and reductions, so that we will briefly mention the most important methods.

**Oxidation.**—The term oxidation, in its narrowest sense, signifies the taking up of oxygen by an element or compound. Thus, on heating ferrous oxide in the air, it is changed into ferric oxide:

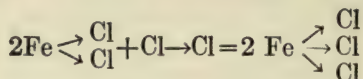


When ferrous oxide is dissolved in hydrochloric acid, the resulting iron compound is called ferrous chloride and, similarly when ferric oxide is dissolved in hydrochloric acid, ferric chloride is formed. Since ferrous salts bear the same relation to ferric salts that ferrous oxide bears to ferric oxide, it is customary to regard as an oxidation the direct conversion of ferrous chloride into ferric chloride, although oxygen itself takes no part in the reaction.



In this last reaction it is evident that the valence of the iron toward chlorine has been increased. According to the electron theory, a molecule is held together by electric charges residing upon the atom. The valence of an atom is due to the number of unit electric charges, called *electrons*, which it possesses. The iron atom in the ferrous chloride molecule has two such electric-charges and these are positive in nature. Each of the chlorine atoms in ferrous chloride possesses a unit charge of negative electricity. In the electrically neutral chlorine molecule, on the other hand, one of the atoms is charged positively and the other

negatively. In ferric chloride, the iron atom has three positive charges and each chlorine atom one negative charge. From the standpoint of positive and negative valences, therefore, the above reaction may be written as follows:



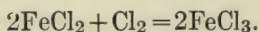
In this equation the arrows are directed from the positively charged atoms toward the negatively charged ones.

*Oxidation involves the increase of the positive valence of an element.*

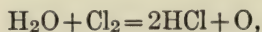
The most important oxidizing agents used in analytical chemistry are:

1. Halogens;
2. Nitric Acid;
3. Hydrogen Peroxide;
4. Potassium Permanganate;
5. Potassium Dichromate.

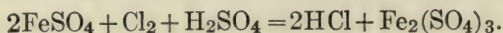
1. The oxidizing action of the halogens depends upon the conversion of the electrically neutral halogen molecule into negatively charged halogen. This may take place by the direct addition of halogen:



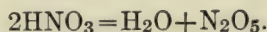
In other cases halogen hydride is formed and either oxygen is set free,



or there is an indirect oxidation whereby some other element gains a positive charge. Thus ferrous sulphate may be converted to ferric sulphate by the action of chlorine and sulphuric acid:

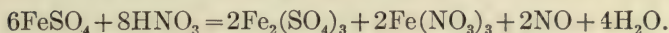
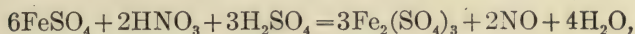
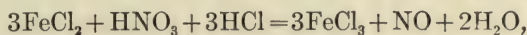


2. The oxidizing action of nitric acid depends upon the reduction of its nitrogen to a lower valence. In nitric acid the valence of the nitrogen is five:



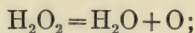


The extent of the reduction of the nitrogen in nitric acid depends upon the nature of the substance to be oxidized; in many cases nitric oxide is formed, but sometimes nitrous oxide, nitrogen or even ammonia results. When a ferrous compound is oxidized by nitric acid, the latter is reduced to nitric oxide, whereby the nitrogen loses three valences and each iron atom gains one. Thus it is clear that one molecule of nitric acid will oxidize three atoms of ferrous iron and it will be necessary moreover to furnish one additional equivalent of some acid for each atom of iron oxidized:

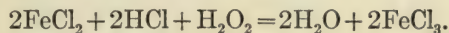


In the last equation only two molecules of nitric acid have been reduced and the remaining six have acted merely as an acid.

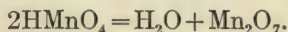
3. The oxidizing action of hydrogen peroxide depends upon its decomposition into water and oxygen:



for example,

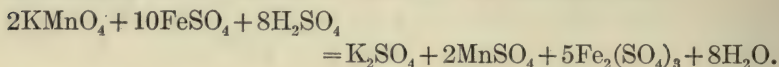


4. The oxidizing action of permanganic acid, or of a permanganate, depends upon the formation of a manganese compound in which the manganese has a lower valence. In the permanganic acid radical the valence of the manganese is seven:



On adding to a nearly colorless acid solution of ferrous sulphate some of the highly colored solution of potassium permanganate, drop by drop, the red color of the permanganate is imparted to the solution only after all the ferrous salt has been changed to ferric salt. In this reaction, the permanganic acid is reduced to manganous salt and this means that the valence of the manganese has been changed from seven to two. Thus each atom of iron gains one valence while each atom of manganese loses

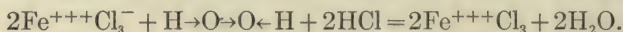
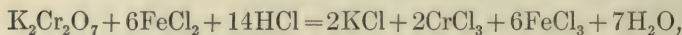
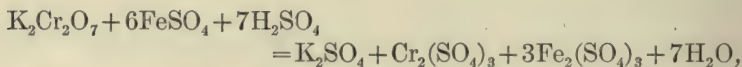
five. To get a whole number of molecules of ferric sulphate. it is necessary to start with an even number of iron atoms. Thus the oxidation of ferrous sulphate by potassium permanganate in sulphuric acid solution is expressed by the equation:



Taking proper precautions it is possible to carry out the same reaction with ferrous chloride in hydrochloric acid solution:



5. The oxidizing action of chromic acid, and of a chromate or a dichromate in acid solution, depends, similarly, upon the reduction of the chromium from a valence of six to a valence of three with the formation of a chromic salt. Thus one atom of chromium will suffice to oxidize three atoms of ferrous iron and it will be necessary to add enough acid to form potassium sulphate, chromic sulphate and ferric sulphate:

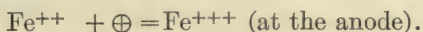
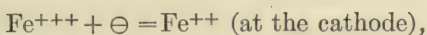


One of the oxygen atoms in  $\text{H}_2\text{O}_2$  possesses one negative and one positive valence.

**Reduction.**—Reduction is the exact opposite of oxidation. Whereas it originally signified simply the withdrawal of oxygen from an element, it has come to include the withdrawal of any other negative element, or radical; or the addition of hydrogen or any other positive element, or radical. In other words, *a reduction involves the decrease of the positive valence of an element.* Oxidations and reductions invariably take place side by side, for whenever one element loses a negative electron, whereby its valence is increased, some other element must gain a negative electron and be reduced. Thus, in the above reactions which were given to illustrate oxidation, there was in each case a reduc-

tion involved. In the case of the halogens, the neutral chlorine molecule\* became negatively charged chlorine in the ferric chloride molecule; the chlorine, therefore, was reduced to chloride. In the hydrogen peroxide molecule one oxygen atom was reduced as a result of the oxidation by hydrogen peroxide. With the permanganate radical, the manganese was reduced, and in the case of chromic acid the chromium was reduced. It would have been equally correct, therefore, to have considered each of the above reactions as representing a reduction.

Oxidations and reductions may be brought about by the direct use of an electric current instead of chemical agents. Thus ferrous salts are oxidized at the positive pole (anode) and ferric salts are reduced at the negative electrode (cathode). If we denote positive electricity at the electrode by the symbol  $\oplus$  and negative electricity by the symbol  $\ominus$ , then electrolytic oxidations and reductions may be represented by equations:

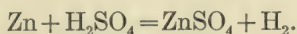


The most important chemicals that are used as reducing agents are:

1. Nascent Hydrogen and Metals;
2. Sulphurous Acid;
3. Hydrogen Sulphide;
4. Stannous Chloride;
5. Hydriodic Acid.

1. Reduction by means of nascent hydrogen, or by metals, may take place in acid, alkaline, or neutral solution.

(a) In acid solution, by the employment of zinc, etc.:



This reaction in itself represents both an oxidation and a reduction, inasmuch as the metallic zinc, which is electrically neutral, becomes changed into zinc with two positive charges which

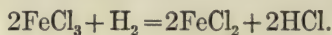
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\* If we consider the neutral chlorine molecule as composed of a negative chlorine atom and a positive chlorine atom, then one chlorine atom is changed from its condition of having one positive charge to that of having one negative charge, which is an algebraic difference of two charges.



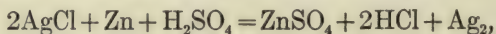
give it power to combine with one  $\text{SO}_4$  group and, on the other hand, the hydrogen in sulphuric acid has lost two charges and become electrically neutral hydrogen. In the last case, we may regard the neutral hydrogen molecule as possessing one positively charged hydrogen atom and one negatively charged hydrogen atom, in which case one atom of the hydrogen molecule has the same charge as in sulphuric acid while the other has not lost only its positive charge, but gained a negative charge, an algebraic difference of two charges.

Now this nascent hydrogen may itself act as a reducing agent and serve for effecting the reduction of some other element, e.g., ferric chloride; in which case the final changes are the oxidation of the zinc and the reduction of the iron:

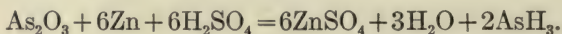


In many cases it is hard to tell whether the reduction process really goes through the stage of forming nascent hydrogen.

By the action of zinc and very dilute sulphuric acid, it is easy to transform silver chloride into metallic silver:

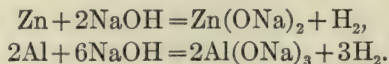


or arsenious anhydride into arsine:



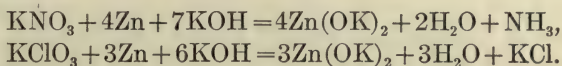
The result of this last equation is the oxidation of zinc from the metallic condition to the bivalent state as represented by zinc sulphate and the reduction of the arsenic which is given three negative charges in place of the three positive valences that each arsenic atom has in  $\text{As}_2\text{O}_3$ . Thus each As atom loses six charges of electricity and each Zn atom gains two, so that it takes six Zn atoms to reduce the two As atoms in  $\text{As}_2\text{O}_3$ .

(b) In alkaline solution, by means of zinc, aluminium, sodium amalgam, or Devarda's Alloy ( $\text{Cu}=50$ ,  $\text{Zn}=5$ ,  $\text{Al}=45$ ). This reaction also may be attributed to nascent hydrogen:

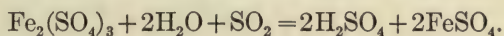


In the case of Devarda's Alloy, the reaction is completed much more quickly than by the use of either zinc or aluminium alone.

Nitrates and chlorates may be reduced in a few minutes by means of Devarda's Alloy and a few drops of sodium hydroxide; the reaction also takes place in neutral solution, but it takes considerably longer:



2. Reduction by means of sulphurous acid takes place in moderately acid solution and depends upon the fact that sulphur is more stable when it has six positive charges, as in sulphuric acid, than when it has only four as in sulphurous acid. Ferric salts are readily reduced by this reagent and since the iron loses only one valence while the sulphur gains two, it is evident that one molecule of sulphur dioxide (the anhydride of sulphurous acid) will reduce two atoms of iron in a ferric salt:

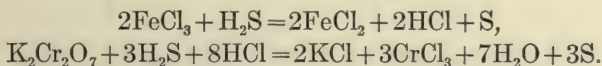


In the same way, arsenic anhydride and many other substances are reduced very readily and completely by means of  $\text{SO}_2$ :



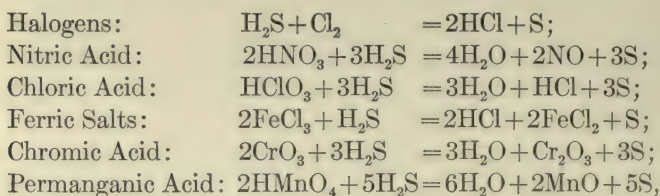
An excess of aqueous sulphurous acid is added to the solution which is to be reduced; it is then heated to boiling; and the boiling is continued while a stream of carbonic acid gas is passed through the solution until the excess of sulphurous acid is driven off.

3. Reduction with hydrogen sulphide, in which the sulphur atom possesses two negative charges, depends upon its oxidation to free sulphur, which is electrically neutral. Thus two atoms of ferric iron are reduced to ferrous iron by one molecule of hydrogen sulphide and one molecule of potassium dichromate reacts with three molecules of hydrogen sulphide:



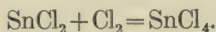
One objection to the use of hydrogen sulphide as a reducing agent is the difficulty involved in the subsequent removal of the precipitated sulphur by filtration. Moreover, hydrogen sulphide is used in qualitative analysis chiefly as a precipitant. If a solution containing an oxidizing agent (such as nitric acid,

chloric acid, chromic acid, etc.), these will be reduced by the hydrogen sulphide with separation of sulphur. The sulphide obtained will be largely contaminated with sulphur, which renders the subsequent examination more difficult. If the solution contains no metal which is precipitated by hydrogen sulphide, but contains oxidizing agents, it will still cause separation of sulphur. One is often in doubt whether there is not some sulphide mixed with the sulphur, and is therefore obliged to examine the precipitate further, which is often unnecessary if the oxidizing agent is previously destroyed. Hydrogen sulphide reduces

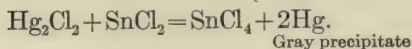
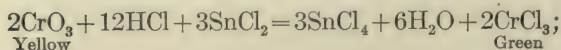
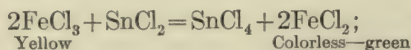


and many other substances.

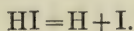
4. Reduction with stannous chloride takes place usually in acid solutions. The reduction depends upon the fact that stannous chloride is readily changed to stannic chloride:



Ferric salts, chromates, permanganates, mercuric salts, and many others are reduced in this way:



5. Hydriodic acid also is a strong reducing agent, the negatively-charged iodine being easily oxidized to neutral iodine:





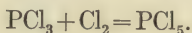
Ferric salts, under certain conditions (see page 13), may be quantitatively reduced in this way to ferrous salts:



As, however, iodine is an oxidizing agent, under other conditions the ferrous salt can be changed back into ferric salt, so that the reduction then will not be quantitative. But it is very important for the analyst to perform all reactions so that they take place as nearly as possible quantitatively. How this may be brought about by changing the conditions of the experiment is shown by

### The Law of Chemical Mass Action.

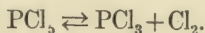
If, for example, we allow chlorine to act upon phosphorus trichloride in the cold, solid phosphorus pentachloride is formed:



If, however, the phosphorus pentachloride is heated, it is decomposed into chlorine and phosphorus trichloride:



The reaction accordingly is *reversible*, which may be represented by writing the equation as follows:



We use, instead of the sign of equality, two arrows pointed in opposite directions, signifying that the reaction may take place in the direction left to right, or from right to left. Similar to phosphorus trichloride, there are a large number of other substances which on heating decompose into their components, and unite again on cooling.

St. Claire Deville (1857) designated this phenomenon *Dissociation*. Ammonium chloride, on volatilization, is dissociated into ammonia and hydrochloric acid, and the dissociation increases with rise of temperature until, at a sufficiently high heat, it is complete. *For every temperature, the ratio of the undissociated to the dissociated part is a constant.*

Let us return to our first example, the phosphorus pentachloride. If we designate by  $[\text{PCl}_5]$  the number of undecomposed gram-mole-



cules of phosphorus pentachloride per liter, by  $[\text{PCl}_3]$  the number of gram-molecules of trichloride, and by  $[\text{Cl}_2]$  the number of gram-molecules of chlorine in the same volume, then the quotient

$$\frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]}$$

is a constant at any definite temperature.

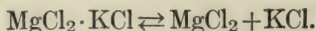
If, therefore, we desire to volatilize phosphorus pentachloride so that the least possible dissociation will take place, the above equation shows us how this may be brought about.

If either  $[\text{PCl}_3]$  or  $[\text{Cl}_2]$  be increased, then in order that the value of the fraction

$$\frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]}$$

remains constant, it is evident that the concentration  $[\text{PCl}_5]$  must become greater; or, in other words, the dissociation of the pentachloride becomes less and there will be practically no dissociation if the pentachloride is volatilized in an atmosphere of phosphorus trichloride or of chlorine. In this way Wurz obtained for the density of phosphorus pentachloride 6.80–7.42, instead of the calculated value 7.2.

Dissociation may be brought about by *solution* as well as by *volatilization*; and in this case the dissociation increases with the *dilution*. For example, if the mineral carnallite ( $\text{MgCl}_2 \cdot \text{KCl} + 6\text{H}_2\text{O}$ ), which occurs at Stassfurt, be dissolved in water and the solution allowed to evaporate until a salt begins to crystallize out, we shall find that instead of obtaining crystals of carnallite we obtain those of potassium chloride. Carnallite is dissociated in aqueous solution into easily soluble magnesium chloride and relatively insoluble potassium chloride which separates out on evaporating:



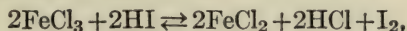
For every concentration the degree of dissociation is a constant.

If we designate by  $[\text{MgCl}_2 \cdot \text{KCl}]$  the number of gram molecules per liter of undecomposed carnallite, by  $[\text{MgCl}_2]$  the number of gram molecules per liter of magnesium chloride, and those of potassium chloride by  $[\text{KCl}]$ , the equation holds:

$$\frac{[\text{MgCl}_2] \times [\text{KCl}]}{[\text{MgCl}_2 \cdot \text{KCl}]} = \text{a constant.}$$

If we wish, therefore, to recrystallize carnallite we must prevent its dissociation by increasing either  $[\text{MgCl}_2]$  or  $[\text{KCl}]$ .\* As a matter of fact, the mineral is recrystallized at Stassfurt from a 23 per cent magnesium chloride solution.

The reduction, mentioned on page 11, of ferric salts by means of hydriodic acid represents, similarly, a reversible reaction:



and for every degree of concentration the following equation holds:

$$\frac{[\text{FeCl}_2]^2 \times [\text{HCl}]^2 \times [\text{I}_2]}{[\text{FeCl}_3]^2 \times [\text{HI}]^2} = \text{a constant.}$$

If we desire to make the reaction take place from left to right quantitatively, the concentration of the hydriodic acid should be increased whereby that of the ferric chloride becomes diminished. In fact, by employing a large excess of  $\text{HI}$  † the ferric salt may be quantitatively reduced to ferrous salt, and this reaction is made use of in the quantitative determination of iron.

This law of Chemical Mass Action was first enunciated by Guldberg and Waage (1867), and holds for all reversible reactions whether they take place by volatilization or by solution.

### Theory of Electrolytic Dissociation.

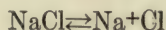
If we insert between the poles of an electric battery a piece of rock salt or some pure distilled water, there will be no electric current in the circuit; a piece of fine platinum wire placed in the circuit will not be made to glow. The solid rock salt, as well as the distilled water, are non-conductors of electricity; they are non-electrolytes. If, however, we dissolve rock salt in distilled water, and

\* In reality an increase of  $[\text{KCl}]$  will not accomplish the desired result, because potassium chloride is more insoluble than either carnallite or magnesium chloride.

† Ferric chloride is to be reduced to ferrous chloride; *i.e.*,  $[\text{FeCl}_3]$  must be made as small as possible. If we wish to oxidize all of the hydriodic acid, then  $[\text{FeCl}_3]$  must be made as large as possible, whereby  $[\text{HI}]$  becomes practically zero.

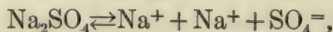
then insert the solution between the poles of the electric battery, the platinum wire will be brought to a bright glow, showing that the salt solution is a good conductor of electricity—an electrolyte. It is thereby proved that by dissolving the non-conducting rock salt in non-conducting water an essential change of the former has taken place. We can make the same observation with all acids, bases, and salts. In an anhydrous state they are non-electrolytes, while in aqueous solution,\* on the other hand, they are electrolytes. These phenomena are readily explained by the theory of electrolytic dissociation proposed by Arrhenius† in 1887. According to this theory, all electrolytes are partially decomposed in aqueous solution into electrically-charged atoms or atom-groups called ions; and the extent of this dissociation increases with dilution, until with very great dilution it is practically complete. For every degree of dilution there exists a certain state of equilibrium between the ions and undissociated molecules.

When the non-electrical rock salt is dissolved in water, it breaks up, according to the equation

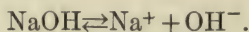


into positively-charged sodium ions and negatively-charged chlorine ions.‡

All salts, acids, and bases behave like rock salt. Thus sodium sulphate decomposes according to the equation



and sodium hydroxide into



By this theory of electrolytic dissociation the phenomena of electrolysis may be explained very simply: If we insert the two poles of a source of electricity into an electrolyte, one of the poles, the anode, is charged with positive electricity, and the other, the cathode, with negative electricity. The electro-positive anode repels the electro-positive ions (cations) and attracts the electro-

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\* They are also electrolytes in the fused state.

† *Z. physik. Chem.* I. p. 631.

‡ Many chemists prefer to designate the positive ions by small dots and the anions by small inclined dashes. The above equation is then written:  $\text{NaCl} \rightleftharpoons \text{Na}^{\cdot} + \text{Cl}'$ .



negative ions (anions); and the latter, as soon as they come in contact with the anode, give up their negative electricity, become neutral and separate out. The same thing happens at the cathode, where the electro-positive ions (cations) are discharged. The amounts of electricity which are neutralized at the electrodes are always renewed by the source of the current, so that the process is continuous.

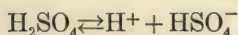
The ions alone are concerned in electrolysis; the undissociated molecules take no part in the process. Just as the transport of electricity through liquids is brought about only by means of the ions, it is likewise true in the majority of cases that it is the ions which cause reactions to take place in aqueous solutions; in fact, the reactions take place more rapidly in proportion to the concentration of the ions. The more ions there are present in a unit of volume the better the solution conducts electricity, because, according to Faraday's law, equivalent ions transport equal amounts of electricity.

If, for example, the conductivity of two acids at the same concentration is as 2:1, it follows that the former acid is twice as strongly dissociated as the latter. The first acid, therefore, will react chemically much more energetically, and for this reason we call it the stronger acid.

The degree of ionization of an electrolyte can be computed from its electrical conductivity.

The strong acids and bases are very largely dissociated, while the weaker acids, such as acetic, carbonic, hydrocyanic, and boric, are dissociated but slightly. This is evident from the table on page 16.

Electrolytes having polyvalent ions undergo a progressive dissociation on being dissolved in water; thus sulphuric acid in concentrated solution is dissociated according to the equation:



into  $\text{H}^+$  and  $\text{HSO}_4^-$  ions and on diluting the solution the latter are gradually dissociated into  $\text{H}^+$  and  $\text{SO}_4^{=}$  ions, so that in dilute solution the following may be present: A small amount of undissociated  $\text{H}_2\text{SO}_4$  molecules,  $\text{H}^+$  ions,  $\text{SO}_4^{=}$  ions, and some  $\text{HSO}_4^-$  ions.

In the case of such weak dibasic acids as carbonic acid or hydrogen sulphide, the second stage of the dissociation is scarcely reached



## Degree of Dissociation of Certain Electrolytes.

## A. ACIDS.

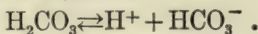
$\frac{N}{10}$ Acid.	Degree of Dissociation.	$\frac{N}{10}$ Acid.	Degree of Dissociation.
$\left. \begin{array}{l} \text{HCl} \\ \text{HBr} \\ \text{HI} \\ \text{HNO}_3 \\ \text{HClO}_3 \\ \text{HClO}_4 \\ \text{HCNS} \end{array} \right\}$	about 90%	$\left. \begin{array}{l} \text{HF} \\ \text{HC}_2\text{H}_3\text{O}_2 \\ \text{H}_2\text{CO}_3 \\ \text{H}_2\text{S} \\ \text{HCN} \\ \text{H}_3\text{BO}_3 \end{array} \right\}$	about 13% " 1.3% " 0.15% " 0.07% " 0.05% " 0.013%
$\text{H}_3\text{PO}_3$	" 44%	$\frac{N}{2} \text{H}_2\text{SO}_4$	" 62%
$\text{HIO}_4$	" 29%	" $\text{H}_2\text{SeO}_4$	" 65%
$\text{H}_3\text{PO}_4$	" 20%	$\frac{N}{32} \text{H}_2\text{C}_2\text{O}_4$	" 20%
		" $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	

## B. BASES.

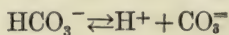
## C. SALTS.

$\frac{N}{10}$ Base.	Dissociation.	Type of Salt $\frac{N}{10}$	Dissociation.
$\text{KOH}, \text{NaOH}$	about 90%	$\text{R}+\text{R}^-$	about 85%
$\text{Ba}(\text{OH})_2$	" 75%	$\text{R}++\text{R}^-$	" 70%
$\text{NH}_4\text{OH}$	" 1.3%	$\text{R}_2+\text{R}^-$	" 70%
		$\text{R}++\text{R}^-$	" 45%

even in quite dilute solutions. Carbonic acid is dissociated chiefly according to the equation

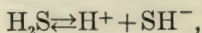


The dissociation



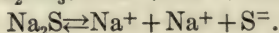
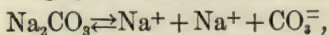
takes place only to an inappreciable extent.

Exactly the same is true of hydrogen sulphide; it is dissociated to some extent according to the equation



whereas the second stage of dissociation hardly takes place at all.

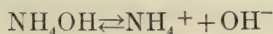
It is altogether different in the case of neutral salts of the weak acids. These are largely dissociated, as follows:



This explains the fact that such weak acids in the free state often show quite different reactions from their salts.

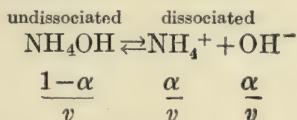
### Influence of Changes in Concentration upon the Dissociation of Electrolytes.

If we assume 1 gram molecule of a weak electrolyte, such as ammonia, to be dissolved in  $v$  liters of solution, the ammonium hydroxide will be partly dissociated according to the equation



into ammonium and hydroxyl ions. If  $\alpha$  gram molecule of the base is dissociated in the sense of the above equation, then the undissociated part will amount to  $1-\alpha$ .

The concentrations per liter are



and according to the *mass-action* law

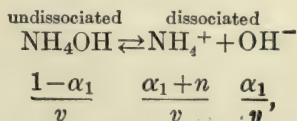
$$k \cdot \frac{1-\alpha}{v} = \frac{\alpha^2}{v^2}$$

$$k = \frac{\alpha^2}{(1-\alpha)v}$$

The constant  $k$  is known as the *dissociation- or affinity-constant*; it is independent of the dilution and is characteristic for every electrolyte. The expression shows, however, that by increasing,  $v$ , or diluting, the fraction of the molecule dissociated ( $\alpha$ ) will be made larger.

If to the solution of the base we add  $n$  additional ammonium ions, by adding solid ammonium chloride, then if  $n$  is considerably larger than  $\alpha$  the degree of dissociation of the base will be greatly diminished, namely, from  $\alpha$  to  $\alpha_1$ , a value which we can readily compute as follows:

In the solution there is present per liter



therefore

$$k = \frac{(\alpha_1+n)\alpha_1}{(1-\alpha_1)v}$$

If  $k$  and  $n$  are known,  $\alpha_1$  can be computed:

$$\alpha_1 = \frac{-(n+vk) \pm \sqrt{(n+vk)^2 + 4vk}}{2}.$$

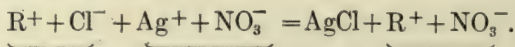
In the case of N/10 ammonia solution the ammonium hydroxide is dissociated only to an extent of 1.32%, the dissociation constant being 0.000018. If we add to 10 liters of this ammonia solution 2 gram molecules of ammonium chloride (107.08 gms.), then since the ammonium chloride is 93% dissociated at this dilution, we are adding  $2 \times 0.93 = 1.86$   $\text{NH}_4$  ions. If this value be inserted in the above equation,  $\alpha_1$  becomes 0.00009; in other words, the dissociation of the ammonium hydroxide is diminished by the addition of the ammonium chloride from 1.32% to 0.009%. The solution now contains so few hydroxyl ions that it will not precipitate solutions of magnesium salts (cf. page 62).

Similarly the dissociation of weak acids is lessened by the addition of their salts. In the case of the stronger acids and bases, the effect of adding a neutral salt to the solution is not so remarkable, because the stronger acids and bases are dissociated to about the same extent as their salts.

### Reactions of the Ions.

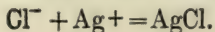
As already mentioned, *most reactions that take place in aqueous solution are reactions between ions.*

When a solution of hydrochloric acid, or of any soluble chloride is treated with silver nitrate solution, a white curdy precipitate of silver chloride is formed:



In the solution at the start there are ions and undissociated molecules present. The electropositive silver ions unite with the electronegative chlorine ions and form electrically neutral silver chloride, which being insoluble is thrown out of solution. This disturbs the equilibrium in the solution, and in order to restore it the reaction between silver and chlorine continues to take place until finally practically all of the chlorine is removed from the solution.

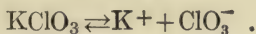
In the above equation, if we remove the R and  $\text{NO}_3$ , which take no part in the reaction, the equation becomes in its simplest form



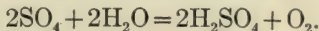
The silver ion is a reagent for detecting the presence of chlorine ions.

All compounds containing chlorine do not react with silver ions to form insoluble silver chloride, but only those which on being dissolved in water yield chlorine ions.

If a solution of potassium chlorate, for example, be treated with silver nitrate solution, there will be no precipitate of silver chloride formed, because the chlorate is not dissociated into chlorine ions, but as follows:



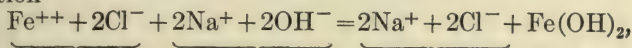
A study of the products obtained on electrolyzing a solution is often a convenient method for determining the species of ions present, but it must be remembered that when certain atomic complexes, such as  $\text{SO}_4$ ,  $\text{NH}_4$ , etc., are set free, they undergo secondary reactions, so that the products obtained on electrolyzing the solution do not correspond to the ions originally present. Thus in the case of the electrolysis of aqueous sulphate solutions the  $\text{SO}_4$  ions, when discharged by the current, decompose water with the evolution of oxygen, and sulphuric acid remains in solution:



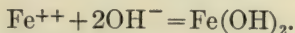
In the same way when ammonium ( $\text{NH}_4$ ) is set free by electrolysis, ammonia and hydrogen are at once formed.

### Complex Ions

We learned on page 2 a characteristic reaction for ferrous salts, namely, the precipitation by means of sodium hydroxide. This reaction is one between ions and takes place according to the equation



or, if we eliminate the ions which take no part,



The hydroxyl ion is a reagent for ferrous ions.

If the insoluble ferrous hydroxide is boiled with potassium cyanide solution it dissolves, forming potassium ferrocyanide,  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . This salt is not a *ferrous* salt and does not give the



characteristic reactions for Fe ions. It is the potassium salt of hydroferrocyanic acid,  $\text{H}_4[\text{Fe}(\text{CN})_6]$ .

On being dissolved in water, the salt undergoes electrolytic dissociation, as follows:



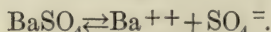
The Fe forms an integral part of the complex ferrocyanide ion; in electrolysis, the latter always migrates to the anode and shows characteristic reactions with different reagents (cf. hydroferrocyanic acid).

Quite a number of such complex ions are encountered in the study of analytical chemistry, and in the formulas given in this book such ions, as a rule, will be enclosed in brackets.

*It is one of the principal tasks of Qualitative Analysis to find out tests for all the ions and to study their separation from one another. It will be our aim to transform these ions into insoluble compounds, into gases, or into characteristically colored compounds.*

### Solubility Product.

When we desire to transform an ion into an insoluble precipitate we must consider how best to carry out the operation. Shall we, in forming insoluble barium sulphate from a solution containing  $\text{SO}_4$  ions add simply an equivalent amount of barium chloride, or shall we add an excess of the reagent? No precipitate is absolutely insoluble in water, so that a little barium sulphate will remain in solution. The solution, however, is then saturated with barium sulphate and contains it chiefly in the form of Ba and  $\text{SO}_4$  ions:



If we designate the concentration of the  $\text{BaSO}_4$  by  $[\text{BaSO}_4]$ , that of the Ba by  $[\text{Ba}]$ , and of the  $\text{SO}_4$  by  $[\text{SO}_4]$ , then for any definite temperature the equation holds:

$$[\text{Ba}] \times [\text{SO}_4] = [\text{BaSO}_4] \times k.$$

If we increase the concentration of the barium ions,  $[\text{Ba}]$ , then the equation shows that  $[\text{BaSO}_4]$  will necessarily become larger, but as the solution is already saturated with barium sulphate this will

result in a further precipitation of the salt. The same end would be attained by the addition of an excess of  $\text{SO}_4$  ions. The product of the concentration of the ions in a saturated solution is known as the *solubility product*.\* When this value has not been reached, the solution will dissolve more of the solid substance. In the case of our precipitates the important rule holds: *to diminish the solubility of a salt it is only necessary to increase the concentration of one of the ions into which the salt dissociates*.

The excess of reagent to be added depends upon the solubility of the precipitate, and upon its tendency to form other atomic complexes. Thus, in precipitating lead or barium sulphates, both of these are soluble in *concentrated* sulphuric acid. They are least soluble in the presence of a *slight* excess of sulphuric acid.†

In order to examine the precipitate further, it must be separated from the solution by means of filtration, and the general rule holds: *The size of the filter should always be governed by the amount of the precipitate and not by the volume of the liquid*. In cases where it is a matter of detecting minute traces, it is often necessary to work with large amounts of the original substance, which requires a correspondingly large amount of liquid to effect solution. If a few milligrams of an unknown body are precipitated from such a solution, and this is filtered off by means of a large filter, it is clear that the tiny precipitate will be spread over the whole of the large filter, which makes it difficult to work with.

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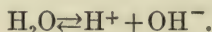
\* It is here assumed that the solubility of the non-ionized salt remains constant. This is not strictly true, for the molecular solubility decreases slightly with increasing concentration of the total dissolved salts. It is known that the ionization of *strong electrolytes* does not conform to the equation given above for  $\text{BaSO}_4$ . In the case of relatively insoluble salts, i.e., in dilute solutions, experiments show that we are justified in assuming the solubility product to be a constant. Here it is assumed that the nature of the solvent remains unchanged and when a solution contains a considerable quantity of any substance, it is not fair to consider that the solution will have precisely the same solvent action as pure water. The principle of the solubility product applies only to very dilute solutions and to fairly insoluble substances.

† In many cases a precipitate is soluble in an excess of the precipitant. Thus potassium hydroxide precipitates  $\text{Zn}(\text{OH})_2$  from a solution of zinc sulphate; an excess of potassium hydroxide dissolves the precipitate, forming  $\text{K}_2[\text{ZnO}_2]$ , which dissociates into  $\text{K}^+$  and  $[\text{ZnO}_2]^-$  ions, and the latter are not precipitated by  $(\text{OH})^-$  ions. This does not contradict the solubility product principle as the  $\text{Zn}^{++}$  ions have disappeared.

Before examining such a precipitate it must be completely freed from all traces of the filtrate. This is accomplished by *washing*. Washing must be continued until no test can be obtained with the wash-water for a certain substance known to be present in the filtrate. For example, suppose we desire to filter off some suspended barium carbonate from a solution containing sodium sulphate; the precipitate must be continuously washed until a sample of the wash-water, acidified with hydrochloric acid, no longer gives a precipitate on the addition of barium chloride. As a rule, it is not advisable to run the wash-water into the filtrate, because this occasions an unnecessary dilution of the latter. The filter must always be smaller than the funnel, and the precipitate should not extend higher than to within 5 mm. of the top of the filter. Finally, large precipitates should be avoided as far as possible, for they render exact work more difficult—filtration and washing consuming too much time.

### Hydrolysis.

Hydrolysis is the name given to the decomposing action of water upon many salts. Corresponding to the fact that water is a poor conductor of electricity, it follows that water is dissociated only to a slight extent.



According to Kohlrausch and Heidweiler,\* the degree of dissociation at 25° C. is  $1.05 \times 10^{-7}$ ; in other words, 10,000,000 liters of water would furnish 1 gram molecule of dissociated water. Small as this is, it suffices to explain the hydrolysis of:

- I. The salts of weak acids with strong bases.
- II. The salts of strong acids with weak bases.
- III. The salts of weak acids with weak bases.

The salts of strong acids with strong bases are not hydrolyzed appreciably.

Hydrolysis is shown to take place by the fact that solutions of neutral salts corresponding to I react alkaline, those of II

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\* Z. phys. chem., 14, 317.



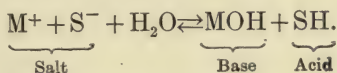
react acid, while those of III are sometimes acid and sometimes alkaline.

The cause of hydrolysis is the action of the ions of water upon the ions of the dissolved salt.

All monobasic salts in aqueous solution are largely dissociated into ions (cf. page 16):



and the phenomenon of hydrolysis may be represented by the general equation



According to the mass-action law

$$K = \frac{[MOH] \times [SH]}{[M] \times [S] \times [H_2O]}.$$

Since the mass of the water in a dilute solution is practically the same both before and after the reaction has taken place, in the above equation  $[H_2O]$  may be left out, and then instead of the constant  $K$  a new value will be obtained:

$$K_h = \frac{[MOH] \times [SH]}{[M] \times [S]}.$$

The base  $MOH$  and the acid  $SH$  are subject to electrolytic dissociation, and the solution will react acid or basic according as to whether the acid or the base is most readily dissociated, i.e., is the stronger.

### *I. Hydrolysis of Salts of Weak Acids and Strong Bases.*

The base formed by the hydrolysis is largely dissociated, while the acid is only slightly ionized. The above equation now takes the form

$$K_h = \frac{[M] \times [OH] \times [SH]}{[M] \times [S]}.$$



Since, however, the extent of dissociation in the case of strong bases is practically equal to that of the salts (cf. page 16) the value  $[M]$  can be cancelled in the numerator and denominator, and we obtain the expression

$$(1) \quad K_h = \frac{[OH] \times [SH]}{[S]} = \frac{[Base] \times [Acid]}{[Salt]}.$$

Owing to the presence of the OH ions in appreciable amount, all salts of this category react alkaline. The alkali salts of hydrocyanic acid, hypochlorous acid, carbonic acid, boric acid, and hydrogen sulphide are of this type.

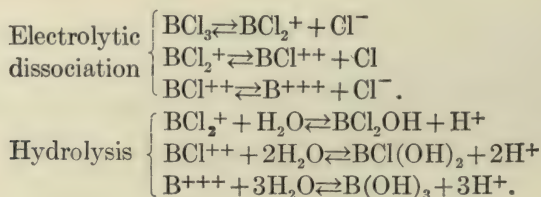
## II. Hydrolysis of Salts of Strong Acids and Weak Bases.

Here the conditions are reversed, and it is the acid which is almost completely dissociated and the base but slightly. In this case the formula becomes

$$(2) \quad K_h' = \frac{[MOH] \times [S] \times [H]}{[M] \times [S]} = \frac{[MOH] \times [H]}{[M]} = \frac{[Base] \times [Acid]}{[Salt]}.$$

Salts of this class, such as those of copper, aluminium, iron, etc., react acid when in aqueous solution.

In the case of polyvalent bases both electrolytic and hydrolytic dissociation take place in stages:



Ferric, aluminium, chromic, and cupric salts, for example, react acid in aqueous solution. If such solutions be evaporated to dryness considerable hydrochloric acid is volatilized, and the residue obtained is an insoluble basic salt which can only be dissolved by means of acid.

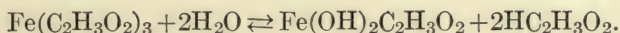
### III. Hydrolysis of Salts of Weak Acids and Weak Bases.

The acids and bases formed by hydrolysis are only slightly dissociated, but to different extents. Our formula becomes

$$(3) K_{h''} = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{M}] \times [\text{S}]} = \frac{[\text{Base}] \times [\text{Acid}]}{[\text{Salt}]^2}.$$

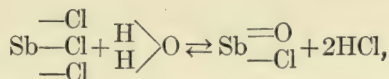
If the electrolytic dissociation of the acid is greater than that of the base, the solution reacts acid; and conversely, when the base is stronger than the acid the solution of the salt shows an alkaline reaction.

Neutral ferric acetate in a *boiling*, aqueous solution is completely hydrolyzed:



Basic ferric acetate is precipitated and can be removed by filtering the hot solution. If the solution is allowed to cool, the reaction tends to take place in the reverse direction and some of the basic salt goes into solution. *Heat and dilution always favor hydrolysis.\**

The hydrolytic action of water, as well as the mass-action law, may be illustrated by the following experiment: A small amount of water is added to a solution of antimony chloride in concentrated hydrochloric acid, causing a heavy precipitation of antimony oxychloride:



which dissolves on adding a little concentrated hydrochloric acid. Further addition of water again precipitates the basic salt, which will dissolve in more of the concentrated acid, etc. It is obvious that by increasing the mass action of the water the reaction goes from left to right, while by increasing the concentration of the hydrochloric acid it goes from right to left.

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\* The ionization constant for water is 0.012 at 25° but rises to 0.015 at 100°. The water is, therefore, much more dissociated at the higher temperature and as a result the hydrolysis is favored.

*Hydrolysis of Salts of Strong Acids with Strong Bases.*

Salts of this type yield, by hydrolysis, acids and bases which are almost entirely dissociated in dilute aqueous solution, and the general equation becomes:

$$K_h''' = \frac{[M] \times [OH] \times [S] \times [OH]}{[M] \times [S]} = [OH] \times [H].$$

The H and OH ions, however, combine to form undissociated water; the solution reacts neutral and contains only as many H and OH ions as correspond to the ionization of water, which is so small that there remains only the electrolytic dissociation of the salt to be considered.

*Salts of this type are not subject to appreciable hydrolysis.*

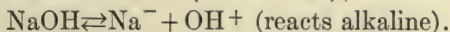
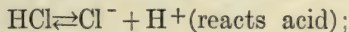
The analytical chemist frequently desires to assist or to prevent hydrolysis. The mass-action principle shows how this can be done. To assist a chemical reaction it is necessary to increase the concentration of one of the original reacting substances or to lessen the concentration of one of the substances formed. Aside from the reactions of oxidation and reduction, all the reactions that take place completely in aqueous solution are those in which the concentration of one of the substances formed is practically negligible. This is due to the formation of (1) a precipitate, (2) a gas, or (3) an undissociated substance. Neutralization takes place between an acid and a base because of the tendency to form undissociated water. Hydrolysis is the reverse of neutralization and is due to the fact that water is slightly ionized. Hydrolysis takes place when one of the products is a gas, a precipitate or an undissociated substance. Thus the hydrolysis of a salt of a weak acid and a strong base is due to the fact that the dissociation of the weak acid is slight. The hydrolysis of a salt of a strong acid and a weak base is due to the formation of the undissociated base. Hydrolysis takes place most readily when both the acid and the base are weak because then both the H ions and the OH ions are removed from the solution to form undissociated acid and undissociated base. Hydrolysis of a salt of a strong acid and a strong base cannot take place because there is then no tendency for the H and OH ions of water to be removed. To assist hydrolysis, boiling is advisable because the water is so much more dissociated at this



temperature than when cold. The reaction that takes place on boiling often proceeds in the other direction on cooling, simply on account of the change in the ionization of the water itself. Dilution favors hydrolysis because it diminishes the concentration of the substances formed; the concentration of the OH ions is not changed, but the relative proportions of OH to other ions present is increased. Hydrolysis is also favored when one of the products is gaseous or insoluble; thus ammonium carbonate is very easily hydrolyzed because both ammonia and carbon dioxide are volatile and ferric acetate is hydrolyzed not only because the acid and base are both weak, but the basic ferric acetate is also very insoluble. Finally, to stop a hydrolysis it is only necessary to add a little free acid or free base at the start and the efficiency of the acid or base is proportional to the extent to which it is itself dissociated. If the solution becomes alkaline as a result of hydrolysis, then a little alkali will best stop hydrolysis, but if the solution becomes acid, a little acid should be added. Moreover, it is advisable to work in cold and concentrated solutions. A dilute aqueous solution of potassium cyanide has the odor of free hydrocyanic acid and reacts alkaline to litmus, but if a little caustic potash is added, the hydrolysis of the salt is prevented and the odor of hydrocyanic acid can be detected no longer. Similarly, boiling a solution of neutral ferric sulphate results in the precipitation of a basic salt, but the precipitation does not take place if a little sulphuric acid is added at the start.

#### Detection of Acids and Bases.\*

For the detection of acids and bases it is customary to employ certain substances which change color on coming in contact with one or the other of the above classes of compounds. The *acid* reaction depends upon the presence of *free hydrogen ions*, while the *alkaline* reaction is caused by *hydroxyl ions*:




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\* The translator has changed the text to conform with the article on The Theories of Indicators, by J. Stieglitz, J. Am. Chem. Soc., **25**, 1112. See also Stieglitz, Am. Chem. J., **39**, and Acree, *ibid.*, **37**, **39** and **42**. Concerning the sensitiveness of indicators, see McCoy, Am. Chem. J., **31**, 508, Salm, Z. phys. chem., **57**, 471, and A. A. Noyes, J. Am. Chem. Soc., **32**, 815.



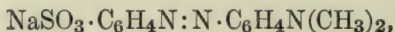
For detecting the presence of acids or alkalis in aqueous solutions we make use of *indicators*; these are substances of organic nature which impart a different color to an alkaline solution than to an acid one. These indicators are, in fact, *pseudo acids* or bases, being very unstable in the form of *free acid* or base, and readily undergo a change of constitution, forming closely allied isomeric substances which are not dissociated. The molecule suffers a rearrangement of its atoms; and it has been found that in the case of all colored organic compounds the color is due to a particular arrangement of atoms called a *chromophor*.

**Methyl orange** is an amphoter and is capable of forming salts with both acids and bases, but its indicator characteristics are due to its very weak basic properties. The neutral solution of its sodium salt is used as an indicator. In this sensitive neutral solution we have a condition of equilibrium between the two isomeric forms of methyl orange as expressed by the equation

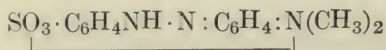
$$\text{HSO}_3\text{C}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_4\text{N}(\text{CH}_3)_2 \rightleftharpoons \text{SO}_3\text{C}_6\text{H}_4\text{NH}\cdot\text{N}:\text{C}_6\text{H}_4:\text{N}(\text{CH}_3)_2.$$

The formula on the left is yellow in color and its color is due to the azo group  $\text{N}:\text{N}$ , while the other compound is red, having for its chromophor the quinoid group  $\text{C}_6\text{H}_4$ :

The sodium salt of methyl orange is yellow and has the formula



and when decomposed by acids the free sulphonate

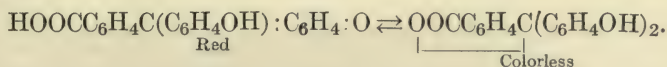


is formed, which is red.

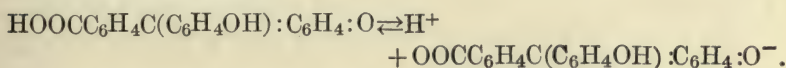
The red quinoid form is ionized as a weak base and forms red salts with acids. It does not form salts readily with weak acids, such as carbonic or acetic acid, because, as we have seen, salts of weak bases and weak acids are hydrolyzed. This is why methyl orange is not a sensitive indicator for weak acids. As a very weak base it will be driven readily out of its red salts by other bases, even weak ones; and the free base will revert again to its yellow form, the result being that methyl orange is an excellent indicator for weak bases.

**Phenolphthalein**, another valuable indicator, is a very weak acid. The free acid, however, is unstable, and when set free from

one of its colored salts reverts instantly into a colorless lactoid form:



The red color is in this case also due to the quinoid grouping :C<sub>6</sub>H<sub>4</sub>:. In the case of the free acid, the condition of equilibrium favors the lactoid form, and only minimal quantities of the quinoid acid are present. This trace of quinoid acid is ionized and in equilibrium with its ions:



The addition of an alkali causes the hydrogen ions to disappear, more of the quinoid molecules must be ionized to preserve equilibrium, and the quinoid molecules in turn be reproduced from the lactoid as fast as the former are converted into the salt. Phenolphthaleïn is a very sensitive indicator towards acids, but on account of being such a weak acid it does not form stable salts with weak bases.

Besides these indicators, others are often employed, among which may be mentioned **Litmus** and **Lacmoid**, which are red with acids and blue with alkalies; and **Turmeric**, which is brown with alkalies and yellow with acids.

## II. REACTIONS IN THE DRY WAY.

These reactions are employed chiefly in the so-called "preliminary examination," in testing the purity of precipitates, and in the examination of minerals. The most important reactions of this nature consist in the testing of a substance with regard to its—

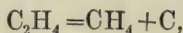
1. Fusibility;
2. Ability to color the non-luminous Bunsen flame;
3. Volatility;
4. Behavior towards oxidation and reduction.

In order to carry out these reactions it is customary to use the non-luminous gas flame; and to understand the operations to be

described it is necessary for us to know something about the composition of illuminating-gas and the nature of the flame.

The illuminating-gas of Zürich averages the following composition:  $\text{CO}_2 = 2.0\%$ ;  $\text{C}_n\text{H}_{2n} = 4.5\%$ ;  $\text{O}_2 = 0.2\%$ ;  $\text{CO} = 8.0\%$ ;  $\text{H}_2 = 48.0\%$ ;  $\text{CH}_4 = 33.0\%$ ; and  $\text{N}_2 = 4.3\%$ .

All of these components, except  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  (which are present only in small amounts), are combustible; they are reducing substances. Illuminating-gas ordinarily burns with a luminous flame, and this luminosity is due to the presence of unsaturated hydrocarbons ( $\text{C}_n\text{H}_{2n}$ ), principally ethylene, propylene, acetylene, benzene, etc. If ethylene is heated to a certain temperature, it is decomposed into methane and carbon:



and it is this glowing carbon which causes the luminosity of the flame.

The other unsaturated hydrocarbons behave like the ethylene. The remaining combustible constituents of illuminating-gas burn with a non-luminous flame. If we bring air into the gas, the flame becomes non-luminous. With the Bunsen burner air is introduced by opening the holes at the base of the burner. In such a gas-flame there are, according to Bunsen, the following parts (Fig. 1 \*):

I. *The inner cone* of the flame, *aab*, in which no combustion takes place, because the temperature here is too low. This part of the flame contains unburned gas mixed with about 62 per cent. of air.

II. *The flame mantle*, indicated by *acaba*, which is composed of burning gas and air.

III. *The luminous tip*, at *b*, which does not appear unless the air-holes are somewhat closed.

In these three principal parts of the flame Bunsen distinguishes **six reaction-zones**:

\* In the drawing, the marks of *d* represent the boundary lines of a metallic chimney, or *flame-protector*, which rest upon the support *ee*. It is advisable to furnish each burner with such a flame protector.



1. *The base of the flame at  $a'$ .* The temperature here is relatively low, because the burning gas is cooled by the constant current of fresh air, and also because the burner itself conducts away considerable heat. This part of the flame serves to test volatile substances to see whether they impart color to the flame. In case several substances are present which color the flame, it is often possible to observe the colors one after the other, in that the most volatile substance colors the flame first, and later the colors caused by the less volatile ones are seen. This would not be possible at a hotter part of the flame, as all of the substances would then be immediately volatilized, producing a mixture of colors.

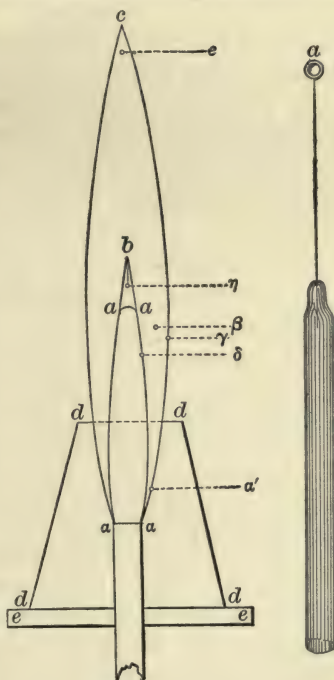


FIG. 1.

2. *The fusing zone at  $\beta$ .* This lies at a distance of somewhat more than one third of the height of the flame, and equidistant from the outside and the inside of the mantle, which is broadest at this part. As this is the hottest part of the flame (about  $2300^{\circ}\text{C.}$ ), it serves for testing substances as to their fusibility and volatility.

3. *The lower oxidizing flame* lies in the outer border of the fusing zone at  $\gamma$ , and is especially suited for the oxidation of substances dissolved in vitreous fluxes.

4. *The upper oxidizing zone*, at  $\epsilon$ , consists of the non-luminous tip of the flame, and acts strongest when the air-holes of the lamp are fully open. It is used for various oxidizing tests, the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at  $\delta$ , in the inner border of the fusing zone next to the dark cone. As the reducing gases are here



mixed with oxygen from the air, many substances which are reduced by the upper reducing flame are here unaffected. This part of the flame is consequently very well adapted for a test which cannot be made with the blowpipe, namely, reduction on the charcoal stick, and in vitreous fluxes.

6. *The upper reducing flame* is at *b*, in the luminous tip of the dark inner cone, which may be produced by gradually diminishing the supply of air. If the luminous tip has been made too large, a test-tube or porcelain dish filled with water and placed over it will be blackened, which should never be the case. This luminous tip contains no free oxygen, is rich in separated incandescent carbon, and has, therefore, a much stronger reducing action than the lower reducing zone. It is used more particularly for the reduction of oxides collected in the form of incrustations.

#### METHODS FOR THE EXAMINATION OF A SUBSTANCE IN THE DRY WAY.

##### 1. *Test of the Fusibility.*

This test is principally made in the examination of minerals, which are introduced into the flame in the loop of a platinum wire (about as thick as a horse-hair). The sample is examined, after heating, by means of a magnifying-glass to see whether the corners are rounded, due to melting. The potentially hottest temperature of the fusing zone amounts to about  $2300^{\circ}\text{C}.$ \* It will never be possible to reach this temperature with the test, because the substance itself loses heat by radiation. As the amount of heat lost by radiation is proportional to the surface exposed, it is evident that we will obtain the maximum heat by using a very small sample and holder. For this reason a coarse wire should not be used for this test.

We distinguish between the following degrees of heat:

1. Faint red glow.....	$525^{\circ}\text{C}.$			
2. Dark red glow .....	$700^{\circ}\text{C}.$	Melting-point of aluminium	$658^{\circ}\text{C}.$ †	
3. Bright red glow .....	$950^{\circ}\text{C}.$	“ silver.....	$955-961^{\circ}\text{C}.$	
4. Yellow glow .....	$1100^{\circ}\text{C}.$	“ gold.....	$1064^{\circ}\text{C}.$	
5. Faint white glow.....	$1300^{\circ}\text{C}.$	“ copper ...	$1064-1084^{\circ}\text{C}.$	
6. Full white glow .....	$1500^{\circ}\text{C}.$	“ platinum .	$1780^{\circ}\text{C}.$	

\* This temperature will be considerably lower with too large a supply of air. According to Naumann, the temperature of illuminating-gas with  $1\frac{1}{2}$  times its volume of air reaches about  $1818^{\circ}\text{C}.$ , but the temperature obtained is usually lower owing to loss by radiation. The finest platinum wire can be melted by means of the flame, but not when it is as thick as a horse-hair.

† Le Chatelier: “High Temperature Measurements.”

Below 525° C. the following substances melt: tin at 232° C., bismuth at 268° C., lead at 327° C., zinc at 420° C.

### 2. *Color Imparted to the Flame.*

The substance (best in the form of the chloride) is placed in the loop of a fine platinum wire, introduced into the base of the flame, and then finally brought into the fusing zone.

### 3. *Oxidation and Reduction in Vitreous Fluxes or Beads.*

To make a bead, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) or salt of phosphorus ( $\text{NaNH}_4\text{HPO}_4 + 4\text{H}_2\text{O}$ ) is used. A piece of very fine platinum wire, about 3 cm. long, is sealed into the end of a glass tube. The wire is heated to redness, and then quickly dipped into the borax or salt of phosphorus, which is held near the flame; whereby a small amount of the salt is fused to the end of the wire. By repeated heating and dipping into the salt a bead of sufficient size is obtained. This should be about 1.5 mm. in diameter at the most. It is not advisable to make a loop at the end of the wire, because in this way the exposed surface is unnecessarily increased. There is no danger of the bead falling off, provided the wire is held horizontally in the flame and the bead is not too large. In order to bring the substance in question into the bead, it is only necessary to moisten the latter with the tongue, and then dip it into the finely-powdered substance, which will cause a small amount to adhere to the bead. It is preferable to introduce too little substance into the bead rather than too much, because, in the latter case, the bead will become dark and opaque. The oxidation of the substance in the bead is brought about by heating it in the lower oxidizing flame; reduction is usually effected by heating in the lower reducing zone, and cooling in the dark inner cone, in order to prevent oxidation, which might take place if the substance were cooled in the air.

In order to clean the wire, a borax bead is produced on the wire, which is then heated, as is shown in Fig. 2, *a*, on one side of the bead only, so that the latter runs along the wire in the opposite direction, dissolving off all impurities. By heating the bead from the other side, Fig. 2, *b*, it is driven toward the end of the wire, from which it can be shaken off by a quick jerk. By repeating this process three times the wire is cleaned with the exception of a small amount of

adhering borax-glass, which can be removed by heating the wire in the fusing zone until the sodium flame entirely disappears.

#### 4. *Reduction on the Charcoal Stick.*

These exceedingly beautiful reactions are among the most sensitive of those used in analytical chemistry, and should be faithfully practised by every beginner. The cause of their sensitiveness is due to their taking place on the extreme end of a tiny piece of charcoal, that is *in a point*, so that the sample has no opportunity to

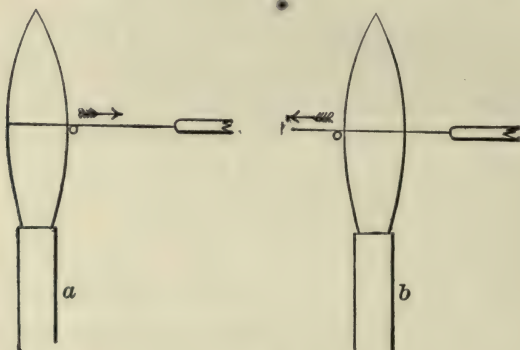


FIG. 2.

spread itself over a large surface, which is the case with the ordinary reactions on charcoal before the blowpipe.

In order to carry out these reactions, we use an ordinary splinter consisting of good, straight fibers, such as used in an old-fashioned brimstone match (not a safety-match, which has already been subject to chemical treatment). It is impregnated with sodium carbonate in the following manner: A crystal of sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) is warmed in the flame, whereby it melts in a part of its water of crystallization. Three-fourths of the length of the match is now smeared with this liquid soda, and the match is then slowly rotated on its axis in the flame, until the soda melts and penetrates the charcoal. On withdrawal from the flame there should be no place which continues to glow; should the latter be the case, the stick should be quickly immersed in the soda again. In this way one obtains a solid little piece of charcoal, which can be heated for a long time without burning through.

In order to carry out a reduction, a small amount of the substance



to be examined is mixed on the palm of the hand with an equal amount of calcined soda, a small drop of melted soda is added, and the mixture is made into a paste by means of the blade of a pen-knife. The warmed piece of charcoal is then rubbed into the mixture, which adheres to it. The sample is first heated in the lower oxidizing flame until it has melted, and then moved into the lower reducing flame. The reduction will be made evident by a violent swelling up of the melt, caused by the evolution of carbon dioxide. As soon as the mass melts quietly the reduction is complete. The substance is allowed to cool in the dark cone, after which it is removed from the flame. The metal is now found on the extreme end of the carbonized match, concentrated in a point. This point is broken off, and triturated with a small amount of water in an agate mortar. The excess of sodium carbonate goes into solution, part of the charcoal floats on the surface of the water, while the heavier metal sinks to the bottom. In case the reduced metal is iron, nickel, or cobalt, it will not be noticeable to the eye, but it may be taken up with a magnetized knife-blade, to which it will adhere, usually mixed with charcoal. This should be dried by cautious warming, the tuft of metal taken off and rubbed between the thumb and forefinger, and then brought into contact with the knife again, to which only the metal will now adhere. The metal is then transferred to a piece of washed filter-paper about 3-4 mm. wide and 50 mm. long, so that it comes as near as possible to the end of the strip. By means of a capillary tube, a drop of hydrochloric acid and one of nitric acid are added, and the paper is warmed over the flame until the black speck (the metal) has disappeared, when the final test can be made.

In order to test for iron, a drop of potassium ferrocyanide is added, whereby the presence of iron is shown by the appearance of a distinct formation of Prussian blue. To test for nickel and cobalt, the metal is dissolved in nitric acid, the excess of acid is evaporated off, and a drop of concentrated hydrochloric acid added, whereby the paper is colored blue if cobalt is present; the nickel shows at the most only a very weak greenish color—usually, however, no color. A little caustic soda solution is now added, and the paper held in the vapors of bromine; in case either nickel or cobalt is present a brownish-black spot appears, due to the formation of either  $\text{Ni}(\text{OH})_3$  or  $\text{Co}(\text{OH})_3$ .

If, however, the metal reduced was malleable, it is usually ob-



tained in the form of a metallic globule on the end of the match, where it can be examined with the aid of a lens. Copper is not always obtained as a globule, but usually as a reddish, sintered mass. By pressing down on malleable metals in the agate mortar they are obtained as a glistening fragment, which can be readily separated from the specifically lighter charcoal by washing. To accomplish this the agate mortar is inclined and a stream of water is directed sideways upon the mass, whereby the charcoal is washed out with the water, and the metal is left clean. It is transferred to a watch-glass and tested as follows:

1. *The Metal is White* (Pb, Sn, Ag, Pt). The metal is treated with a few drops of nitric acid and carefully warmed. Lead and silver dissolve readily, particularly upon addition of a little water. Silver will be detected by the addition of a drop of hydrochloric acid, whereby white silver chloride, soluble in ammonia, is precipitated. The test for lead is dilute sulphuric acid, which precipitates white lead sulphate.

If the metal, on treatment with nitric acid, remains unchanged, it is probably platinum. It should be dissolved in aqua regia, evaporated to dryness, dissolved in a little water, and potassium chloride solution added. A yellow, crystalline precipitate confirms the presence of platinum. If the metal, when treated with nitric acid, becomes changed into a white insoluble oxide, it is tin. In this case, another fragment of metal is dissolved in concentrated hydrochloric acid and tested for tin by means of mercuric chloride solution, or bismuth oxide and caustic soda.

2. *The Metal is Yellow to Red* (Cu, Au). Copper is readily dissolved in nitric acid, and the solution gives with potassium ferrocyanide a reddish-brown precipitate. Gold is insoluble in nitric acid, but soluble in aqua regia. The evaporated solution gives a violet-brown color with stannous chloride, due to finely-divided gold.

### Reduction in a Glass Tube.

Besides the borax bead and the charcoal stick, reduction is often effected by means of metallic sodium, potassium, or magnesium.

Thus small amounts of phosphorus in anhydrous salts may be detected in the following manner: The substance to be tested is placed in a glass tube, 3 mm. wide and 50 mm. long, which is closed

at one end. A small cylinder of potassium or sodium (freed from petroleum by rubbing between filter-paper), or even a piece of magnesium wire, is added to the tube, and the contents then heated until the glass itself begins to soften. The reaction is so violent that the substance seems to take fire. After cooling, the tube is broken in a porcelain mortar, when, by breathing over the mass, the smell of phosphoretted hydrogen may be detected.

The halogens, sulphur, and nitrogen are tested for in a similar way, as will be shown later.

### Reduction in the Upper Reducing Flame for the Purpose of forming Metallic and Oxide Incrustations.

The volatile elements which are reducible by means of hydrogen or charcoal may be detected in this part of the flame with the greatest ease, as, for example, arsenic, antimony, cadmium, bismuth, selenium, and tellurium. The metallic incrustations are obtained by holding in one hand a small portion of the substance on a thin asbestos thread (platinum will be attacked) in the upper reducing zone of a small gas-flame, where the oxide is reduced to volatile metal, and burned in the upper oxidizing flame to oxide. In the other hand, closely over the substance to be tested, is held a glazed porcelain evaporating-dish, filled with water, as is indicated in Fig. 3 at *B*. The metallic vapors are condensed by the cold dish, and deposited on it in the form of a metallic mirror or film. If, however, the dish is held above the upper oxidizing flame (at *A*), there is formed a thin, often invisible, oxide incrustation on the bottom.

Should it be necessary to treat the metallic incrustation with a large amount of solvent (as is necessary in the detection of selenium and tellurium), the porcelain dish is replaced by a test-tube half filled with cold water. A somewhat larger test-tube is used to hold the solvent, and the smaller test-tube, on which the incrustation was deposited, is placed within the larger tube and the liquid warmed if necessary.

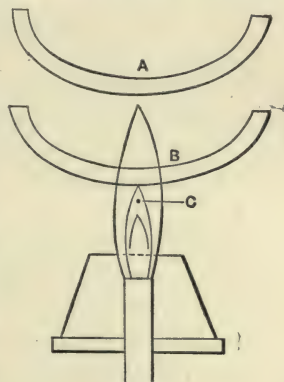


FIG. 3.

placed within the larger tube and the liquid warmed if necessary.

### Blowpipe Reduction on Charcoal.

These tests are made in the so-called "preliminary examination." For this purpose a small cavity is made with a penknife in a piece of good charcoal (preferably of linden wood), in which a knife-bladeful of the substance to be tested is placed, previously mixed with twice as much anhydrous sodium carbonate. As charcoal is a porous body, it will readily absorb easily fusible substances, like the alkalies. Other substances are changed, by means of the sodium carbonate used, into carbonates, which are, for the most part, decomposed, on heating, into oxides and carbon dioxide. The oxides of the noble metals are decomposed, without the aid of the charcoal, into oxygen and metal; while those of the remaining metals are either reduced to metal or remain unchanged. Thus  $\text{CuO}$ ,  $\text{PbO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ , and  $\text{CoO}$  are reduced either to a fused metallic globule ( $\text{Pb}$ ,  $\text{Bi}$ ,  $\text{Sb}$ ,  $\text{Sn}$ ,  $\text{Ag}$ , and  $\text{Au}$ ), or to a sintered mass of metal ( $\text{Cu}$ ), or to a glistening metallic fragment ( $\text{Fe}$ ,  $\text{Ni}$ ,  $\text{Co}$ ,  $\text{Pt}$ ). The oxides of zinc, cadmium, and arsenic do not give metallic globules, but are, however, easily reduced to metal. These metals are so volatile that they are changed into vapors, and are carried from the reducing zone of the flame into the oxidizing zone, where they are changed into difficultly-volatile oxides. These oxides, which have characteristic colors, are then deposited on the charcoal outside the cavity.

Zinc gives an incrustation which is yellow while hot, and white when cold; that of cadmium is brown; while the oxide of arsenic gives a white and readily volatile incrustation. Furthermore, the volatilization of arsenic gives rise to a characteristic garlic odor. The metals lead, bismuth, and tin give, besides the metallic globule, an oxide incrustation which is typical.

At the same time, nitrates, nitrites, chlorates, etc., may be recognized by the fact that they cause a very rapid combustion of the glowing charcoal (deflagration). This deflagration is not to be confused with a decrepitation which takes place on heating substances containing enclosed moisture or gases, such as rock salt, fluor-spar, etc. Crystals of such substances are burst by the quick expansion of the enclosed liquid, and scattered about.

Many difficultly-fusible substances do not melt into the charcoal. Thus many silicates form a bead with the soda, which only after



*continuous* heating will give up the alkali and allow it to be absorbed by the charcoal, leaving behind the white infusible silica. Phosphates and borates act similarly, only these do not leave behind an oxide, but a fused glass. Infusible white oxides, as those of calcium, strontium, magnesium, aluminium, and many of the rare earths (Welsbach mantle, for example), glow very brightly, and in fact more brightly as they are more strongly heated.

### Division of the Metals into Groups.

We may divide the metals, for purposes of analytical chemistry, into five groups:

The *First Group* contains those metals whose *chlorides are insoluble*, or difficultly soluble, and whose sulphides are insoluble, in dilute acids. They may, therefore, be precipitated from their solutions by means of either hydrochloric acid or hydrogen sulphide.

The *Second Group* contains those metals whose chlorides are soluble, but whose *sulphides are insoluble* in dilute acids. They may be precipitated from their solutions by means of hydrogen sulphide, but not with hydrochloric acid.

The *Third Group* contains those metals whose *sulphides are soluble in dilute acids*, but are insoluble in water and alkalies; and also those metals whose sulphides are hydrolytically decomposed into hydrogen sulphide and metallic hydroxide. The members of this group are precipitated completely by *hydrogen sulphide only from alkaline solutions*.

The *Fourth Group* contains those metals whose sulphides are soluble in water, but whose *carbonates are insoluble in the presence of ammonium chloride*. They are precipitated by *ammonium carbonate* in the presence of ammonium chloride, but not by any of the above reagents.

The *Fifth Group* contains magnesium and the alkalies; they are not precipitated by any of the above reagents.

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In order to carry out an analysis with certainty it is necessary to understand not only the reactions of the different elements, but we must know as well the *sensitiveness* of each reaction. The analyst should be able to draw a conclusion by the size of the precipitate formed as to the approximate amount which is present in



the original substance. This, however, is possible only when the experiments are made with known amounts. *Consequently we take reagents of a known strength, and allow them to act on known amounts of the different substances.* According to the suggestion of R. Blochmann \* it is well to make the solutions of the different reagents either double-normal, normal, half-normal, or tenth-normal. For many years the author has used in his laboratory solutions of reagents and salts according to this principle, and has found that the beginner in this way gets a far better understanding of the stoichiometrical relations than when solutions of almost any concentration are used, as was formerly the custom.

By a normal solution we understand one which contains in one liter one gram-equivalent of the substance in question, referred to a gram atom of hydrogen as a unit. A tenth-normal solution will contain one tenth of a gram-equivalent in a liter, etc.

Thus one liter of a normal solution will contain

HCl	=	36.46	grams, equivalent to one gram-atom of hydrogen.						
$\frac{\text{H}_2\text{SO}_4}{2}$	=	$\frac{98.08}{2}$	= 49.04	grams, equivalent to one gram-atom of hydrogen.					
$\frac{\text{H}_3\text{PO}_4}{3}$	=	$\frac{98.03}{3}$	= 32.68	"	"	"	"	"	"
NaOH	=	40.06		"	"	"	"	"	"
$\frac{\text{KMnO}_4}{5}$	=	$\frac{158.11}{5}$	= 31.62	"	"	"	"	"	"
$\frac{\text{K}_2\text{Cr}_2\text{O}_7}{6}$	=	$\frac{294.4}{6}$	= 49.08	"	"	"	"	"	"

The great advantage of this system is that one always knows how much of one solution should be used in order to react with another quantitatively. Thus 1 cc. of a normal caustic soda solution will neutralize 1 cc. of any normal acid, or 2 cc. of any half-normal acid. In the same way 1 cc. of a normal solution of sulphuric acid, or of any sulphate, will precipitate quantitatively the barium from 1 cc. of a normal barium chloride solution.

## THE MOST COMMON LABORATORY REAGENTS.

### I. CONCENTRATED ACIDS.

	Sp. Gr.	Per Cent Acid by Weight.
1. Hydrochloric acid.....	1.189	37.9
2. Nitric acid.....	1.386	62.6
3. Sulphuric acid.....	1.840	96.0

\* Berichte, 1890, 31.

II. DILUTE ACIDS,  $\frac{2}{1}$  NORMAL.

1000 c.c. contain:

1. Hydrochloric acid.....	72.92	grams
2. Nitric acid.....	126.04	"
3. Sulphuric acid.....	98.08	"
4. Acetic acid.....	120.06	"
5. Tartaric acid.....	150.05	"

III. ALKALIES,  $\frac{2}{1}$  NORMAL.

1000 cc. contain:

1. Sodium hydroxide.....	80.12	grams
2. Potassium hydroxide.....	112.32	"
3. Ammonium hydroxide.....	70.10	"
4. Conc. Ammonia (sp. gr. 0.905) contains 27% $\text{NH}_3$ .		

## IV. SALTS.

(a)  $\frac{2}{1}$  Normal.

1000 cc. contain:

1. Ammonium carbonate.....	96.08	grams
2. Ammonium chloride.....	106.98	"
3. Sodium carbonate.....	106.10	"
4. Ammonium sulphide.....	—	

(b) Normal.

1000 cc. contain:

1. Sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ ).....	136.12	grams
2. Sodium phosphate ( $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ ) $\frac{358.35}{3}$ .....	119.43	"
3. Sodium hypochlorite ( $\text{NaOCl}$ ) $\frac{74.5}{2}$ .....	37.25	"
4. Sodium nitrite ( $\text{NaNO}_2$ ) 69.06.....	69.06	"
5. Potassium nitrite ( $\text{KNO}_2$ ) 85.16.....	85.16	"
6. Potassium bichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) $\frac{294.5}{6}$ .....	49.08	"
7. Calcium chloride ( $\text{CaCl}_2 + 6\text{H}_2\text{O}$ ) $\frac{219.10}{2}$ .....	109.50	"
8. Magnesium sulphate ( $\text{MgSO}_4 + 7\text{H}_2\text{O}$ ) $\frac{246.56}{2}$ .....	123.27	"
9. Barium chloride ( $\text{BaCl}_2 + 2\text{H}_2\text{O}$ ) $\frac{244.34}{2}$ .....	122.17	"
10. Ferric chloride ( $\text{FeCl}_3$ ) $\frac{162.25}{3}$ .....	54.08	"
11. Potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$ ) $\frac{422.6}{4}$ .....	105.6	"
12. Lead acetate ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$ ) $\frac{379.00}{2}$ .....	189.50	"
13. Stannous chloride ( $\text{SnCl}_2 + 2\text{H}_2\text{O}$ ) $\frac{225.93}{2}$ .....	112.97	"

14. Mercurous nitrate ( $\text{Hg}_2(\text{NO}_3)_2$ )	$\frac{524.02}{2}$	262.01 grams
15. Cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ )	$\frac{291.2}{2}$	145.6 "

(c)  $\frac{1}{2}$  Normal.

1000 cc. contain:

1. Ammonium oxalate ( $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$ )	$\frac{142.10}{4}$	35.53 grams
2. Mercuric chloride ( $\text{HgCl}_2$ )	$\frac{270.9}{4}$	67.73 "
3. Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ )	$\frac{248.30}{2}$	124.15 "
4. Sodium bromide ( $\text{NaBr} + 2\text{H}_2\text{O}$ )	$\frac{139.04}{2}$	69.52 "
or ( $\text{NaBr}$ )	$\frac{103.01}{2}$ *	51.50 "
5. Potassium cyanide ( $\text{KCN}$ )	$\frac{65.16}{2}$	32.58 "
6. Potassium iodide ( $\text{KI}$ )	$\frac{166.12}{2}$	83.06 "
7. Potassium sulphocyanate ( $\text{KCNS}$ )	$\frac{97.22}{2}$	48.61 "
8. Potassium arseniate ( $\text{KH}_2\text{AsO}_4$ )	$\frac{180.17}{6}$	30.03 "
9. Zinc sulphate ( $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ )	$\frac{287.6}{4}$	71.9 "
10. Manganese sulphate ( $\text{MnSO}_4 + 4\text{H}_2\text{O}$ )	$\frac{223.12}{4}$	55.78 "
11. Nickel sulphate ( $\text{NiSO}_4 + 7\text{H}_2\text{O}$ )	$\frac{280.9}{4}$	70.22 "
12. Cadmium sulphate ( $3\text{CdSO}_4 + 8\text{H}_2\text{O}$ )	$\frac{769.51}{12}$	64.12 "
13. Copper sulphate ( $\text{CuSO}_4 + 5\text{H}_2\text{O}$ )	$\frac{249.74}{4}$	62.44 "
14. Chrome alum ( $\text{CrK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ )	$\frac{499.61}{6}$	83.26 "
15. Alum ( $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ )	$\frac{474.56}{6}$	79.09 "
16. Bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 + 5\text{H}_2\text{O}$ )	$\frac{484.11}{6}$	80.69 "

\* Sodium bromide crystallizes with two molecules of water from a solution which is not above  $30^\circ$ ; from hotter solutions the salt crystallizes in the anhydrous condition.



(d)  $\frac{1}{10}$  Normal.

1000 cc. contain:

1. Uranyl acetate ( $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O}$ )  $\frac{424.58}{20}$  ..... 21.23 grams
2. Silver nitrate ( $\text{AgNO}_3$ )  $\frac{169.94}{10}$  ..... 16.99 "

## V. SATURATED SOLUTIONS.

100 grams solution contain at  $15^\circ \text{C}.$ :

1. Hydrogen sulphide..... 0.48 grams  $\text{H}_2\text{S}$
2. Barium hydroxide..... 5.95 "  $\text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O}$
3. Lime water..... 0.13 "  $\text{CaO}$
4. Calcium sulphate..... 0.26 "  $\text{CaSO}_4 + 2\text{H}_2\text{O}$
5. Chlorine water ..... 0.73 "  $\text{Cl}$
6. Bromine water..... 3.66 "  $\text{Br}$

In the author's laboratory these solutions are prepared in five-liter amounts. In order to do this as quickly as possible, and with sufficient accuracy for qualitative purposes, flasks are used which contain five liters when filled up to a mark on the neck. Similarly, in weighing out the substance, tares are used, containing shot, which give the weight of substance that should be dissolved in five liters.

In the preparation of the dilute acids and ammonia, small cylinders are used, which are so etched that the correct amount of commercial acid can be measured out therein, and this is then diluted to five liters.

Thus

278 cc. conc. sulphuric	acid will make 5 liters 2 N. acid.
726 cc. " nitric	" " " 5 " 2 N. "
809 cc. " hydrochloric	" " " 5 " 2 N. "
1922 cc. 30% acetic	" " " 5 " 2 N. "
698.5 cc. conc. ammonia	" " " 5 " 2 N. "

## Determination of the Sensitiveness of Reactions.

The more sensitive a reaction is, the smaller will be the amount of the substance which can be detected in a given volume, in a definite time, with the reagent in question. Let us assume that the amount of substance taken is dissolved in 100 cc. of liquid the time allowed to be two or three minutes, and the limit of sensitiveness to be the smallest amount of substance which can be detected under these conditions.

A few examples will make the method clear:

Magnesium salts are precipitated by means of sodium phosphate, in the presence of ammonium chloride and ammonia, in the form of magnesium ammonium phosphate. What is the sensitiveness of this reaction? We take 1 cc. of our normal magnesium sulphate solution, add three drops of ammonium chloride solution, and two or three drops of ammonia and sodium phosphate solution; the characteristic white precipitate is formed immediately. We dilute, now, the normal solution of magnesium sulphate ten times, and repeat the experiment with 1 cc. of the diluted solution. The result will be—

1 cc. of N. Mg solution,	100 cc. = 1.2	gram. Mg, reacts immediately.
1 cc. " $\frac{N}{10}$ Mg	" 100 cc. = 0.12	" Mg, " "
1 cc. " $\frac{N}{100}$ Mg	" 100 cc. = 0.012	" Mg, " "
1 cc. " $\frac{N}{1000}$ Mg	" 100 cc. = 0.0012	" Mg, " after a few seconds.
1 cc. " $\frac{N}{10000}$ Mg	" 100 cc. = 0.00012	" Mg, " after one to two minutes.

If, therefore, 100 cc. of a solution contain 0.00012 gram Mg, the magnesium can be detected within from one to two minutes. Should the detection of smaller amounts be desired, the solution must be concentrated by evaporation.

This reaction can be called very sensitive. The following potassium reactions are much less delicate:

(a) *Reaction with Chloroplatinic Acid* (page 47).

1 cc. of  $\frac{N}{5}$  KCl solution, 100 cc. = 0.78 gm. K, reacts with a drop of  $H_2PtCl_6$  immediately.

1 cc. of  $\frac{N}{50}$  KCl solution, 100 cc. = 0.078 gm. K, does not cause precipitation within three minutes.

1 cc. of  $\frac{N}{25}$  KCl solution, 100 cc. = 0.156 gm. K, does not cause precipitation within three minutes; but does, however, on addition of two drops of alcohol.

1 cc. of  $\frac{N}{16.7}$  KCl solution, 100 cc. = 0.234 gm. K, reacts immediately on stirring.

The sensitiveness of the reaction lies, therefore, between 0.156 and 0.234 gm. K per cc. In order to detect smaller amounts of potassium than 0.156–0.234 gm. per 100 cc., the solution must be strongly concentrated by evaporation.

(b) *Reaction with Tartaric Acid* (page 48).

1 cc. of  $\frac{N}{5}$  KCl solution, 100 cc. = 0.78 gm. K, reacts immediately with two drops of sodium acetate and two drops of a concentrated solution of tartaric acid.

1 cc. of  $\frac{N}{50}$  KCl solution, 100 cc. = 0.078 gm. K, reacts after one to two minutes with vigorous shaking.

This can be taken as the limit of sensitiveness.

If the beginner will test the delicacy of all reactions in this way, he will quickly get a clear insight into the solubility relations of the different salts.



## REACTIONS OF THE METALS (CATIONS).

WE begin with the metals of the Fifth Group, because a knowledge of their reactions is necessary in order to understand the reactions of the other groups.

### GROUP V. ALKALIES.

POTASSIUM, K; SODIUM, Na; AMMONIUM,  $\text{NH}_4$ ; (CÆSIUM, Cs; RUBIDIUM, Rb; LITHIUM, Li).

The metals of this group decompose water at the ordinary temperature with evolution of hydrogen and formation of strongly alkaline-reacting hydroxides, which cannot be freed from their hydrate water even on fusion. The pure oxides ( $\text{R}_2\text{O}$ ) are difficult to prepare, cautious heating of the metal in the air forming peroxides at the same time. The salts of these metals are colorless for the most part, and readily soluble in water. Of these salts the carbonates, the tertiary and secondary phosphates, the cyanides, and the borates react alkaline in aqueous solution (hydrolysis). The salts of the alkalies are more or less volatile and impart to the non-luminous flame characteristic colors.

**POTASSIUM, K.** At. Wt. 39.10.

Sp. Gr. 0.87. M. Pt. (Melting-point)  $62.5^\circ \text{C}$ .

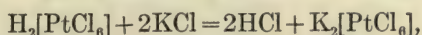
*Occurrence.*—Sylvite ( $\text{KCl}$ ), isometric, and carnallite ( $\text{MgCl}_2, \text{KCl} \cdot 6\text{H}_2\text{O}$ ) orthorhombic, occur at Stassfurt in the presence of halite and anhydrite. Saltpetre ( $\text{KNO}_3$ ), orthorhombic prisms. Further, in very many silicates, *e.g.*, monoclinic feldspar ( $\text{KAlSi}_3\text{O}_8$ ), and muscovite ( $\text{KH}_2\text{Al}_3\text{Si}_3\text{O}_{12}$ ); also in plants in the form of organic salts, which yield on combustion potassium carbonate (potash).

#### REACTIONS IN THE WET WAY.

Potassium forms very few salts that are difficultly soluble in water. The chloroplatinate, acid tartrate, and perchlorate are the

least soluble, and are consequently used in the detection of potassium.

1. **Chloroplatinic Acid** \* ( $\text{H}_2[\text{PtCl}_6]$ ) gives in concentrated solutions a yellow precipitate of potassium chloroplatinate,



which consists of small regular octahedra (visible with a magnifying-glass). In case the potassium solution is not very concentrated, no precipitation may appear at first; but on rubbing the sides of the beaker or test-tube with a glass rod the formation of the precipitate will be hastened.

This is always the case when a crystalline precipitate is formed. The solution is supersaturated before the precipitate separates out, and the formation of crystals is hastened by the mechanical shock.

The behavior of the potassium chloroplatinate on ignition is very characteristic; it is decomposed into chlorine, platinum, and potassium chloride:



If the products of ignition are treated with water, and the platinum filtered off, the filtrate will again give with chloroplatinic acid the yellow crystalline precipitate of  $\text{K}_2[\text{PtCl}_6]$ . (Note difference from ammonium chloroplatinate.)

*Solubility of the Potassium Chloroplatinate in Water.*

100 parts of water dissolve:

At	0° C. ....	0.70 parts	$\text{K}_2[\text{PtCl}_6]$
	10° C. ....	0.90	" "
	20° C. ....	1.12	" "
	100° C. ....	5.18	" "

In a saturated KCl solution, or in 75 per cent alcohol, the precipitate is practically insoluble.

For this reaction it is best to use the chloride. The addition of chloroplatinic acid to potassium iodide solution causes a deep-

---

\* Platinic chloride,  $\text{PtCl}_4$ , gives no precipitate with potassium salts, or at least only after long standing. The above reagent, chloroplatinic acid, is a dibasic acid, and is obtained by dissolving platinum in aqua regia. The solution is prepared of such strength that there are ten grams of platinum in every 100 cc.

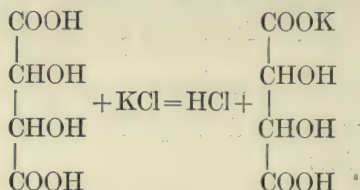
reddish-brown color due to the formation of the soluble salt  $K_2[PtI_6]$



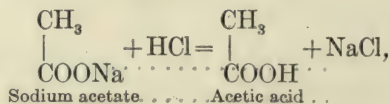
Similarly, potassium cyanide is not precipitated by chloroplatinic acid owing to the formation of complex platinum-cyanogen compounds.

In case we desire to test an iodide or cyanide for potassium, the salt should first be changed to chloride by evaporation with concentrated hydrochloric acid.

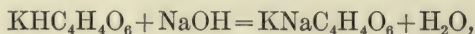
2. **Tartaric Acid** ( $H_2C_4H_4O_6$ ) produces, in not too dilute neutral solutions of potassium salts, a white crystalline precipitate of potassium acid tartrate (orthorhombic, hemihedral):



The potassium acid tartrate is readily soluble in mineral acids, but difficultly soluble in acetic acid and water; 100 parts of water at 10° C. dissolve 0.425 gm. of this salt. If sodium acetate is added to the solution, the mineral acid set free by the reaction will be replaced by acetic acid:



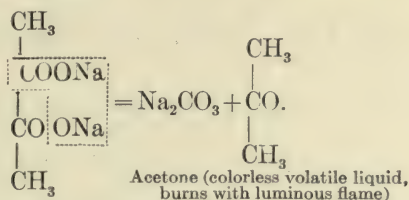
whereby the reaction is made much more sensitive. Rubbing the sides of the dish will also hasten the formation of the precipitate. It is not advisable to neutralize the mineral acid with caustic soda; for if the latter is added till the solution is neutral, sodium-potassium tartrate (Rochelle salt) will be formed,



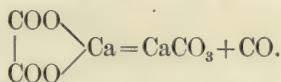
which, like all neutral tartrates, is readily soluble in water; so that no precipitation will take place. On igniting the acid potassium tartrate, empyreumatic vapors (smelling like burnt sugar) are given off, and carbon and potassium carbonate are left behind. If the



mass is now moistened with hydrochloric acid, it will froth strongly. This is a property not only of potassium tartrate, but is common to *all salts of organic acids*. On ignition they are changed into carbonates, and when the acid is non-volatile, carbonization takes place; but with volatile acids there is at the most only a slight carbonization. With many metals the carbonate is not left unchanged; frequently it is broken up into carbon dioxide and oxide of the metal; in the case of salts of organic acids with reducible metals, the metal itself is left with the carbon. Thus sodium acetate will yield sodium carbonate and acetone, with only a slight carbonization:



On gentle ignition, calcium oxalate yields calcium carbonate and carbon monoxide; the latter burns with a blue flame.

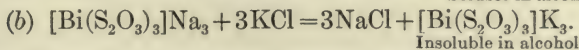
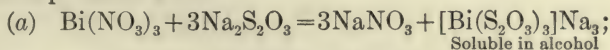


On strong ignition, the calcium carbonate is decomposed into lime and carbon dioxide:



Tartrates of lead, iron, and many other metals on being ignited yield carbon and metal.

**3. Bismuth-Sodium Thiosulphate** (Carnot's\* reaction).—If half-normal bismuth nitrite solution is mixed with two or three drops of half-normal sodium thiosulphate solution and 10–15 cc. of absolute alcohol are added (turbidity being cleared by the cautious addition of water), this solution will cause a precipitation of yellow potassium-bismuth thiosulphate when added to a solution of a potassium salt:

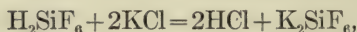



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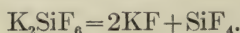
\* Z. anal. Chem., 1897, 512.

The presence of ammonium chloride prevents the reaction.\*

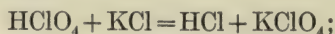
4. **Hydrofluosilicic Acid** ( $\text{H}_2\text{SiF}_6$ ), added in considerable excess to a solution of a potassium salt, precipitates gelatinous potassium silicofluoride,



which is difficultly soluble in water and dilute acids and insoluble in alcohol. On heating, it is decomposed into volatile silicon fluoride, and potassium fluoride remains behind:

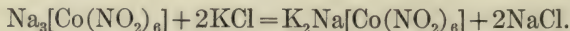


5. **Perchloric Acid** ( $\text{HClO}_4$ ) precipitates white, crystalline potassium perchlorate,



100 parts of water dissolve at  $0^\circ$  0.07 parts  $\text{KClO}_4$ , and at  $100^\circ$  19.8 parts  $\text{KClO}_4$ .

6. **Sodium Cobaltinitrite.** ( $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ ) precipitates yellow potassium-sodium cobaltinitrite:



Ammonium salts give a similar precipitate, but moderate amounts of alkaline-earth elements or of lithium do not interfere.

The reagent may be prepared by dissolving 100 gms.  $\text{NaNO}_2$  in 200 cc. water, adding 60 cc. of 30 per cent acetic acid and 10 gms.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . After standing a day or more, the solution is filtered and diluted to 400 cc.

The presence of 0.3 mgm. of potassium may be detected within ten minutes.† The test must not be made in alkaline solution or  $\text{Co}(\text{OH})_3$  will be precipitated.

#### REACTIONS IN THE DRY WAY.

Potassium compounds color the non-luminous flame violet. The presence of very small amounts of sodium conceals the violet

\* Private communication from W. Wislicenus.

† William C. Bray, Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 39.

potassium flame. If, however, the flame is viewed through cobalt glass or indigo solution, the reddish-violet potassium rays pass through, while the yellow sodium rays are completely absorbed.

*Flame Spectrum.*—Potassium gives a characteristic flame spectrum. A double red line,  $769.9 \mu\mu$  and  $766.5 \mu\mu$ , (appearing as a single line with weaker dispersion), and a faint violet line,  $404.4 \mu\mu$ , appear at comparatively low temperatures. With a hotter flame, other lines are visible in the yellow,  $583.2 \mu\mu$ ;  $580.2 \mu\mu$  and  $578.2 \mu\mu$ , and in the green,  $535.1 \mu\mu$  and  $511.3 \mu\mu$  (see chart, Frontispiece).

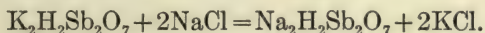
### SODIUM, Na. At. Wt. 23.00.

Sp. Gr. 0.97. M. Pt.  $95.6^\circ \text{C}$ .

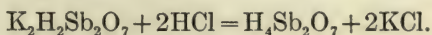
*Occurrence.*—Sodium occurs very extensively in nature. Its most important mineral is halite, rock salt ( $\text{NaCl}$ ), isometric system. It is found in very large deposits often quite pure, but usually contaminated with clay, anhydrite, and gypsum, and is present in large amounts in the ocean, and in many salt springs. Sodium also occurs in nature in the form of carbonate, as thermonatrite ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), orthorhombic; natron or soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), monoclinic; trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), monoclinic; as nitrate in Chili saltpetre, or soda nitre ( $\text{NaNO}_3$ ), hexagonal, rhombohedral; as cryolite ( $\text{Na}_3\text{AlF}_6$ ), triclinic; in many silicates as albite ( $\text{NaAlSi}_3\text{O}_8$ ), triclinic; and as tinkal, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), monoclinic.

#### REACTIONS IN THE WET WAY.

1. **Potassium Pyroantimonate\*** ( $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) produces in neutral or weakly alkaline solutions of sodium salts a heavy, white, crystalline precipitate, which is formed more quickly by rubbing the sides of the vessel with a glass rod:



The test must not be made in an acid solution, for in that case an amorphous precipitate of pyroantimonic acid will be formed:




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\* For the preparation of this reagent see page 240.



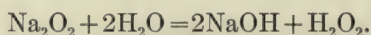
Furthermore, no other metals than the alkalis should be present because they also cause precipitates—amorphous ones for the most part.

2. **Tartaric Acid and Chloroplatinic Acid** do not precipitate sodium salts, the sodium salts of these acids being readily soluble in water. Sodium chloroplatinate is of an orange color, and is readily soluble in 75 per cent alcohol (note difference from potassium).

### **Sodium Peroxide, $\text{Na}_2\text{O}_2$ .**

This substance, which is now used commercially on account of its energetic oxidizing power, is obtained by burning dry sodium in the air as a heavy, yellow powder, and shows the following characteristic reactions:

*Behavior toward Water.*—If a little water is added to some of this substance in a test-tube, a considerable amount of heat will be set free, and oxygen gas will be given off (sufficient to ignite a glowing splinter\*). Water decomposes the sodium peroxide, according to the equation



But on account of the heat of the reaction a part of the hydrogen peroxide is decomposed into water and oxygen.

If warming up of the solution is avoided (which can be done by throwing the sodium peroxide in small portions into ice-water), it will dissolve, with scarcely any evolution of oxygen, to a clear, strongly alkaline liquid, which gives, as before, all the reactions of hydrogen peroxide.

If some sodium peroxide is placed on a watch-glass under a bell-jar and near an evaporating-dish containing water, the sodium peroxide in twelve hours will completely change over to a pure white hydrate ( $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O}$ ), which will dissolve in water without decomposition at the ordinary temperature.

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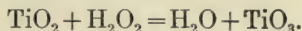
\* This will sometimes cause an explosion, because the commercial product often contains metallic sodium, which with water forms hydrogen; thus both hydrogen and oxygen are set free at the same time, and the glowing splinter may then cause an explosion. (Private communication from E. Constan.)

## Reactions of Hydrogen Peroxide.

### (a) In Acid Solution.

If the solution obtained by the action of water on sodium peroxide is used for these tests, it must be acidified with dilute sulphuric acid, care being taken to keep the solution cool.

1. **Titanium Sulphate** gives a distinct yellow color, caused by the formation of pertitanic acid,



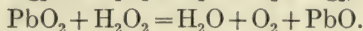
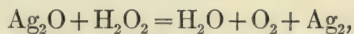
This is the most delicate test for hydrogen peroxide. The titanium sulphate solution for this reaction may be prepared by fusing one part of commercial titanium dioxide with 15–20 parts of potassium pyrosulphate and dissolving the fusion, after cooling, in cold, dilute sulphuric acid.

2. **Chromic Acid.**—If the acid solution of hydrogen peroxide is shaken with a little ether (free from alcohol) and a trace of potassium dichromate is added, after which the mixture is again shaken, the upper layer of ethereal solution will be colored a beautiful blue, owing to the formation of chromium peroxide.\*

3. **Permanganic Acid** in acid solution will be decolorized, with evolution of oxygen:



Similar to the permanganate, many other oxides are reduced by hydrogen peroxide, with evolution of oxygen; *e.g.*,  $\text{Ag}_2\text{O}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ ,  $\text{MnO}_2$ , etc.:

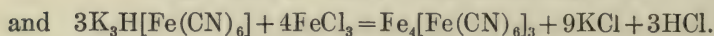
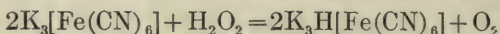


4. **Potassium Ferricyanide and Ferric Chloride.**—If a trace of potassium ferricyanide is added to a very dilute and almost neutral

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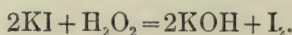
\* This test is very sensitive and will detect as little as one-tenth milligram of  $\text{H}_2\text{O}_2$ . In carrying out this test, a *blank* test must always be tried with the ether and alcohol alone because the former will often give the test. Ether after standing in the air is likely to contain some ethyl peroxide,  $(\text{C}_2\text{H}_5)_4\text{O}_3$ , which gives the test. It is possible to free the ether from this peroxide by letting it stand over night in contact with sodium and then redistilling it.

solution of ferric chloride, so that the solution appears a distinct yellow, and an almost neutral solution of hydrogen peroxide is then added, the mixture will soon assume a green tint, and finally, on standing, Prussian blue will separate out. The potassium ferricyanide is reduced by the hydrogen peroxide to potassium ferrocyanide, which forms Prussian blue with the ferric chloride.



According to Schönbein, the smallest traces of hydrogen peroxide may be detected by this reaction ( $\frac{2}{1000}$  mg.  $H_2O_2$  per liter). As, however, many other substances ( $SnCl_2$ ,  $SO_2$ , etc.) will reduce potassium ferricyanide to potassium ferrocyanide, this reaction alone cannot always be relied on.

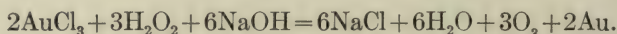
5. **Starch Paste and Potassium Iodide.**—If to an acid solution containing starch paste and potassium iodide some hydrogen peroxide is added, a blue color will at once appear:



By means of this reaction,  $\frac{5}{1000}$  mg. per liter of hydrogen peroxide may be detected.

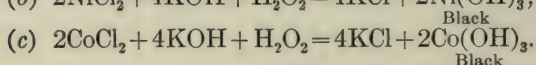
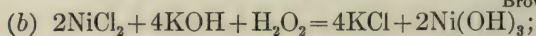
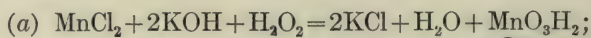
(b) *In Alkaline Solution.*

1. **Gold Chloride** by means of hydrogen peroxide at ordinary temperatures will be reduced to metal, with evolution of oxygen. The gold usually separates in a very finely-divided state, and appears brown by reflected light and greenish blue by transmitted light:



If very dilute gold solutions are used, the metal sometimes separates out in the form of a yellowish film adhering to the sides of the test-tube.

2. **Salts of Manganese, Nickel, and Cobalt** give dark-colored precipitates:



Brown

Black

Black



Hypochlorites give the same reactions with manganese, nickel, and cobalt salts, but they do not give the reaction with gold chloride.

### Ozone, $O_3$ .

Ozone is always formed when oxygen is exposed to the silent electric discharge; it is often present in oxygen that has been prepared electrolytically and, according to Brunck, is present to some extent in the gas prepared by ignition of potassium chlorate. Ozone is a strong oxidizing agent and behaves in many respects like hydrogen peroxide, with which it is often confused. Ozone may be distinguished from hydrogen peroxide as follows:

1. Ozone does not give a yellow coloration with titanium sulphate solution.
2. Ozone does not cause precipitation of gold from its solutions.
3. Ozone sets free iodine immediately from dilute, neutral potassium iodide solution.
4. Ozone liberates bromine from an acid solution of sodium bromide.
5. Ozone causes bright metallic silver to at once assume a steel-blue tint.

The sensitiveness of this last reaction is remarkable if carried out according to the directions of Manchot and Kampeschulte. A bright piece of silver foil on being heated to about  $240^\circ$  and then exposed to the action of ozone shows the immediate formation of steel-blue spots with violet edges. This reaction does not take place with pure silver in the cold. If, however, the silver is polished by rubbing with emery paper, the reaction will then take place in the cold. Traces of iron oxide are left upon the silver from the emery and the oxide catalyzes the reaction. Other oxides,  $Ag_2O$ ,  $CoO$ ,  $NiO$ ,  $Bi_2O_3$ ,  $Pb_3O_4$ ,  $V_2O_5$ ,  $MnO_2$ ,  $CuO$ ,  $ThO_2$ ,  $CeO_2$ ,  $TiO_2$ ,  $WO_3$ ,  $U_3O_8$ , and to a less degree  $MoO_3$ ,  $HgO$ ,  $CaO$  and  $BaO$ , also have the same effect. Thus if the silver is etched with nitric acid and is then dried, it will react with ozone in the cold.

The principal reactions of sodium are the

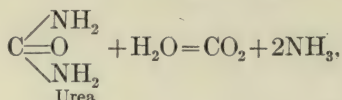
## REACTIONS IN THE DRY WAY.

Sodium salts color the non-luminous gas-flame a monochromatic yellow, which can be readily distinguished from the yellow flame of the gas in the following way: If we illuminate an orange-colored body (such as a stick of sealing-wax or a crystal of potassium dichromate) with white light (all glowing solid bodies emit white light), the red and orange rays will be reflected: the body appears orange. If these bodies are illuminated with the monochromatic sodium light, they can now only reflect yellow light: the bodies appear yellow (a delicate test).

*Flame Spectrum.*—A yellow double line ( $589.6 \mu\mu$  and  $587.0$ ), coinciding with the D-line of the sun's spectrum. This is an extremely delicate reaction; the  $\frac{1}{10,000,000}$  part of a milligram of sodium can be recognized in the spectrum.

**AMMONIUM,  $\text{NH}_4$ . At. Wt. 18.04.**

*Occurrence.*—In small amounts as carbonate and nitrite in the air. As ammonium chloride it is found in the fissures of active volcanoes. Ammonium derivatives are formed by the decay of many organic substances containing nitrogen: albumin, urea, etc.,



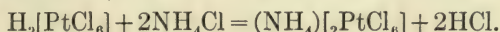
and in a similar way by the dry distillation of many nitrogenous substances, such as coal, horn, hair, etc.

Although ammonium itself is known only in the form of its amalgam, yet we are justified in considering it as a metal, in the first place because the electrolysis of ammonium salts causes the setting free of the cation  $\text{NH}_4(\text{NH}_3 + \text{H})$  at the same time that the corresponding anion is set free; and, further, because the ammonium salts are isomorphous with potassium salts.

## REACTIONS IN THE WET WAY.

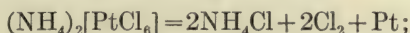
Ammonium salts show in many reactions a striking similarity to potassium salts.

1. **Chloroplatinic Acid** gives a yellow crystalline precipitate:

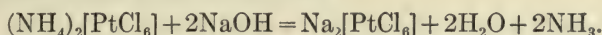


This salt may be distinguished from the potassium salt—

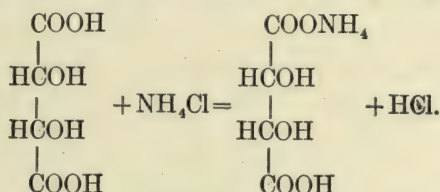
- (a) by its behavior on ignition; platinum alone is left behind:



- (b) by its behavior on treating with strong bases, whereby the smell of ammonia may be detected:



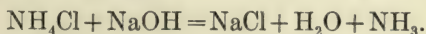
2. **Tartaric Acid** produces, as with potassium, a white, crystalline precipitate of ammonium acid tartrate. The addition of sodium acetate, and rubbing the sides of the glass vessel with a stirring-rod, will hasten the formation of the precipitate:



The ammonium acid tartrate, like the corresponding potassium salt, is soluble in alkalis and mineral acids. It may be distinguished from the potassium salt by its behavior on ignition, carbon alone being left behind, and the residue not effervescing with hydrochloric acid; furthermore, it will give off ammonia on heating with caustic soda solution.

3. **Sodium Cobaltinitrite** gives a yellow precipitate similar to that produced with potassium. Before testing for potassium with this reagent, therefore, it is necessary to expel ammonium salts by evaporating the solution to dryness in a porcelain dish and heating until no more fumes are evolved.

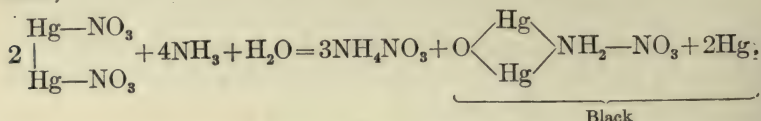
4. **Caustic Alkalies** ( $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{Ca}(\text{OH})_2$ ) decompose ammonium salts in a boiling solution setting free ammonia gas:



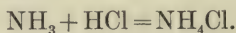
It is much safer to test for ammonium in this way than to attempt the formation of a precipitate with the above reagents. With this test all ammonium salts will give off ammonia, recogniz-



able by its odor, or by its ability to turn mercurous nitrate paper black,



Ammonia is also recognized by its turning red litmus paper blue, or by causing dense fumes of ammonium chloride if a glass rod moistened with concentrated hydrochloric acid is held in contact with the ammonia vapors:



The above-mentioned reactions are not suitable for the detection of very small amounts of ammonia, to the extent, for example,

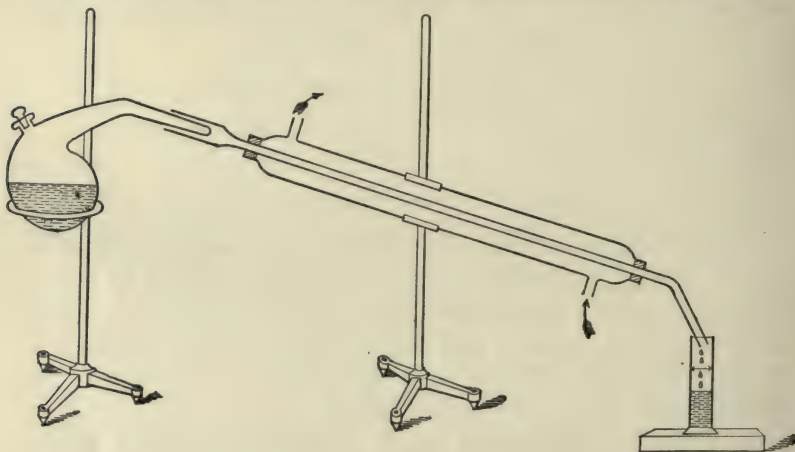
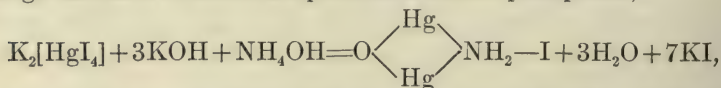


FIG. 4.

that it occurs in drinking-water. In such a case Nessler's reagent is used (an alkaline solution of potassium mercuric iodide). Large amounts of ammonia produce a brown precipitate,



of enormous coloring power, so that the minutest trace of ammonia can be recognized by the formation of a distinct yellow color in the solution. In order to detect the presence of ammonia in drinking-water with the help of this reaction, we proceed as follows:

First of all, the apparatus (Fig. 4) must be freed completely

from all traces of ammonia. To accomplish this, about 500 cc. of spring water is placed in the retort (whose neck is bent as in the illustration), 1 cc. of a boiled, saturated soda solution is added, and the solution is distilled. The end of the retort's neck is pushed into the condenser tube; it is best not to use a rubber connector here, as the condensed water serves to make a sufficiently tight connection.

The distillation is continued until 50 cc. of the distillate, placed in a small 50 cc. graduate of white glass, will show no sign of a yellow color after adding 1 cc. of the Nessler solution, stirring, and letting it stand for a quarter of an hour. The apparatus is now ready for the experiment proper. The retort is emptied of its contents, 500 cc. of the water to be tested is introduced, 1 cc. of the saturated soda solution is added, and 50 cc. distilled off. The distillate is treated with 1 cc. of Nessler's reagent and stirred. With large amounts of ammonia a yellow color will immediately be noticeable, which on standing becomes orange, while with very large amounts of ammonia a brown precipitate appears. If only traces are present, the solution will assume a yellow tint only after standing some time.

The Nessler's reagent \* which is used for this experiment is prepared as follows: 6 gms. of mercuric chloride are added to 50 cc. of water (which must be absolutely free from ammonia †), and solution is effected by warming to 80° C. in a porcelain dish; 7.4 gms. of potassium iodide are dissolved in 50 cc. of water, added to the above, and the mixture allowed to cool. The clear liquid is then poured off and the residue washed three times with 20 cc. of cold water, in order to dissolve out as much of the chloride as possible. Then 5 gms. more of potassium iodide are added, which causes the mercuric iodide to go into solution. The solution is now poured into a 100-cc. flask, 20 gm. KOH dissolved in a little water are added, and the contents of the flask diluted to 100 cc. When

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\* Cf. L. W. Winkler, *Zentralbl.*, 1899, II, p. 320.

† Water absolutely free from ammonia, commonly called "best water," is prepared from ordinary distilled water, or good spring water, by adding some soda and distilling. The first portion of the distillate, which always contains ammonia, is rejected until Nessler's reagent, applied as above to 50 cc. of the distillate, gives a negative test, which will be after about one-fourth of the original amount of water has been distilled off. The portion now coming off will be completely free from ammonia, and is used for the preparation of the reagent. The distillation, however, must be stopped when about five-sixths of the water has been distilled, as the remainder may contain ammonia owing to the decomposition of organic substances in the water by the strongly concentrated soda solution.

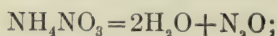
the solution has completely cleared, it is carefully decanted into a clean flask and kept in the dark.

#### REACTIONS IN THE DRY WAY.

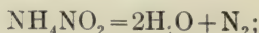
The behavior of ammonium salts on heating in a closed tube is very characteristic.

*All ammonium salts, except those with non-volatile acids, are completely volatilized, partly without and partly with decomposition.* The non-volatile acids whose salts form an exception to this rule are boric, phosphoric, chromic, molybdic, tungstic, and vanadic acids.

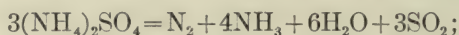
Only the salts with the halogen acids are volatile without decomposition; they give a white sublimate.\* Most ammonium salts which suffer decomposition on ignition split off water. Thus the nitrate gives water and nitrous oxide,



the nitrite gives water and nitrogen,

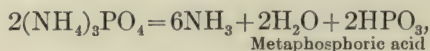


the sulphate gives water, nitrogen, ammonia, and sulphur dioxide,



the oxalate gives water, considerable ammonia, carbon dioxide, carbon monoxide, and, towards the end of the reaction, dicyanogen, which is best recognized by its odor.

With regard to ammonium salts with non-volatile acids, the behavior of the phosphate and the dichromate may be mentioned:



The chromic oxide remains as a voluminous mass, looking very much like green tea. Ammonium salts do not impart a very characteristic color to the flame; the border of the flame is tinged slightly greenish.

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\* There is really a dissociation into  $\text{NH}_3$  and halogen hydride, but unless special pains are taken to separate these dissociated products, they unite to form a sublimate of the original compound.

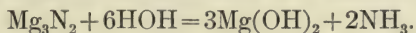


**MAGNESIUM, Mg.** At. Wt. 24.32.

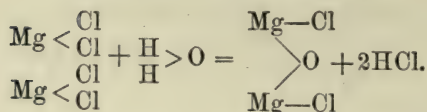
Sp. Gr. = 1.75. M. Pt. = 632.6° C.

*Occurrence.*—Magnesium compounds are found very abundantly in nature. The most important minerals are magnesite,  $\text{MgCO}_3$ , rhombohedral, isomorphous with calcite; dolomite,  $(\text{Ca}, \text{Mg})\text{CO}_3$ ; brucite,  $\text{Mg}(\text{OH})_2$ , rhombohedral; carnallite,  $\text{KMgCl}_3$ , orthorhombic; kieserite,  $\text{MgSO}_4 + \text{H}_2\text{O}$ , monoclinic; epsomite,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , orthorhombic; spinel,  $\text{MgAl}_2\text{O}_4$ , isometric, isomorphous with magnetite,  $\text{Fe}_3\text{O}_4$  and with chromite,  $\text{FeCr}_2\text{O}_4$ . Magnesium also occurs in a great many silicates. Thus almost all the minerals of the olivine group contain more or less magnesium. To this group belong forsterite,  $\text{Mg}_2\text{SiO}_4$ , monticellite,  $\text{CaMgSiO}_4$ , and olivine,  $(\text{FeMg})\text{SiO}_4$ , all orthorhombic. An important decomposition product of the olivine minerals is serpentine,  $\text{Mg}_3\text{H}_4\text{Si}_2\text{O}_9$ . Almost all the minerals of the pyroxene-amphibole group contain magnesium: augite,  $\text{MgAl}_2\text{SiO}_6$ , hornblende,  $\text{CaMg}_2\text{Al}_2\text{Si}_3\text{O}_{12}$ , and tremolite,  $\text{CaMg}_3\text{Si}_4\text{O}_{12}$ , all three forming monoclinic crystals. Asbestos is a variety of tremolite with very fine fibers. Meerschaum is a magnesium silicate of the composition  $\text{H}_4\text{Mg}_2\text{Si}_3\text{O}_{10}$ , and is quite similar to talc,  $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$ , sometimes called steatite.

*Properties of Magnesium.*—Magnesium is a silver-white metal. It decomposes water very slowly, forming an oxide ( $\text{MgO}$ ) which is only slightly soluble in water, with a weakly alkaline reaction. Magnesium reacts directly with nitrogen at 300° C., forming magnesium nitride ( $\text{Mg}_3\text{N}_2$ ), which is readily decomposed by water, forming magnesium hydroxide and ammonia:



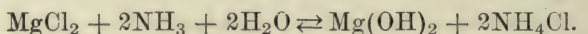
The salts of magnesium are almost all colorless and soluble in water. The hydroxide, carbonate, phosphate, arseniate, and arsenite are insoluble. The sulphide, which can be prepared only in the dry way, is completely decomposed by water into hydroxide and hydrogen sulphide (hydrolysis). If an aqueous solution of magnesium chloride be evaporated to dryness on the water-bath, there is no hydrolytic decomposition, the residual salt,  $\text{MgCl}_2 + 6\text{H}_2\text{O}$ , dissolves in water, forming a perfectly clear solution. On heating the chloride containing the water of crystallization to 106° and higher, however, a considerable amount of hydrochloric acid fumes escape and a basic magnesium chloride insoluble in water is left behind:



When a saturated solution of magnesium chloride is mixed with magnesium oxide, the mixture soon solidifies, forming a mass hard as stone known as *magnesia cement*, consisting of magnesium oxychloride.

#### REACTIONS IN THE WET WAY.

**1. Ammonia.**—In a neutral solution containing no ammonium salts, ammonia produces a white, gelatinous precipitate of magnesium hydroxide. The precipitation, however, is never quantitative; in dilute solutions when only a slight excess of ammonia is used only a slight precipitate is formed, but on increasing the excess of ammonia, more and more magnesium is thrown out of solution until finally the greater part of the magnesium, although never all of it, is changed to the insoluble hydroxide. The behavior of magnesium compounds towards ammonia is quite different in case the solution already contains a considerable amount of ammonium salts; ammonia then causes no precipitation in the cold even when it is added in great excess; in the latter case, part of the magnesium will precipitate on boiling the solution. The reaction takes place according to the following equation:



In the presence of considerable ammonium salts the reaction takes place in the sense of the equation from right to left and in fact quantitatively; on the other hand, the presence of an excess of ammonia serves to increase the tendency of the reaction to take place in the direction from left to right, while the ammonium chloride formed will invariably cause the reaction to cease before all of the magnesium is precipitated.

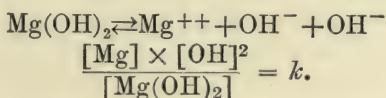
As we shall find later on, solutions containing bivalent metals of the ammonium sulphide group behave in precisely the same way towards ammonia as those of magnesium, whereas the trivalent metals of this group act differently. The latter are precipitated completely as hydroxides\* by ammonia from solutions containing

\* With the exception of uranium, which is precipitated as ammonium uranate.

their salts even when only a slight excess of the reagent is used, and in spite of the presence of ammonium salts.

Why does magnesium behave so differently from aluminium, ferric iron, etc.? Loven has answered this question and shown it to be due to the different solubility products of the hydroxides in question.\*

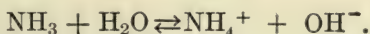
Magnesium hydroxide is appreciably soluble in water, enough dissolving to make the water react alkaline. When magnesium hydroxide is suspended in water, the solution is saturated with it and the dissolved hydroxide is almost completely dissociated:



If we increase the concentration of  $[\text{OH}]$ , the above equilibrium will be disturbed, and to offset this some undissociated magnesium hydroxide will be formed. Since the solution is already saturated with the latter compound, this means that magnesium hydroxide will be precipitated from the solution.

If, however, we diminish in any way the concentration of the hydroxyl ions, that of the magnesium hydroxide will likewise decrease in accordance with the above equation, because the only way to restore equilibrium is for magnesium hydroxide to dissolve; if sufficient hydroxyl is removed finally all of the precipitate will disappear.

The solubility product of magnesium hydroxide being relatively large, an appreciable amount of hydroxyl ions is required to precipitate it from solutions. The hydroxyl ions may come from ammonia according to the equation



Ammonia, however, is dissociated only slightly in aqueous solution, and furthermore the concentration of the hydroxyl ions is greatly diminished if we increase the concentration of the ammonium ions by adding an ammonium salt. There will then be extremely few hydroxyl ions in solution.†

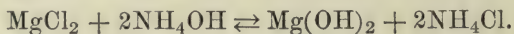
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\* Z. anorg. Chem. **11** (1896), p. 404.

† Cf. page 18.



On treating a solution of magnesium chloride with ammonia, the hydroxyl ions from the latter will cause the precipitation of magnesium hydroxide:



At the same time, however, ammonium chloride is formed so that the concentration of the ammonium ions is increased, and this tends to prevent the further dissociation of ammonia and the precipitation of magnesium.

In fact, by adding ammonium chloride to a solution in which magnesium hydroxide is suspended, the concentration of the hydroxyl ions is diminished so that the solubility product of magnesium hydroxide is no longer reached and the ammonium chloride solution exerts a solvent action upon the hydroxide.

The bivalent metals of the ammonium sulphide group, as mentioned above, act similarly to magnesium in this respect. Trivalent iron and aluminium, on the other hand, are precipitated quantitatively by a slight excess of ammonia even in the presence of ammonium salts because the hydroxides of these metals are almost entirely insoluble, and, moreover, the bases are so weak that the electrolytic dissociation is relatively slight, or in other words their solubility products are so low that they are exceeded even by the small amount of hydroxyl ions into which ammonia dissociates in the presence of considerable ammonium chloride.

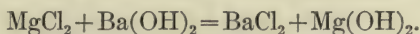
Formerly, the non-precipitation of magnesium by ammonia in the presence of ammonium salts was explained by the assumption that complex salts such as  $[\text{MgCl}_3]\text{NH}_4$  and  $[\text{MgCl}_4](\text{NH}_4)_2$  were formed, but Lovén\* has shown that this is not the true explanation; there is no evidence of the formation of any such salt under the given conditions.

Inasmuch as magnesium, ferrous iron, Mn, Ni, Co, and Zn are not precipitated by ammonia in the presence of ammonium salts, we have a means for separating these from the remaining metals of the ammonium sulphide group (ferric iron, Al, Cr, Ti, U). If the separation takes place in a hot solution more ammonium chloride is required to prevent the magnesium from precipitating than in the cold.

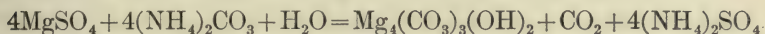
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\* Z. anorg. Chem. **11** (1896), p. 404. See also Treadwell, Z. anorg. Chem. **37** (1903), p. 326; Herz, *ibid.*, **38** (1903), p. 138.

2. **Barium Hydroxide** precipitates magnesium almost quantitatively as hydroxide from its solutions, but only in the absence of ammonium salts:



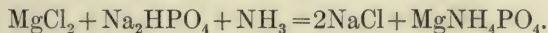
3. **Ammonium Carbonate** precipitates, in the absence of other ammonium salts, a basic salt (usually only on boiling or after long standing). The composition of the precipitated salt varies with the temperature and the concentration of the solution, the following salt being often obtained:



In a cold, concentrated solution containing an excess of ammonia and some alcohol, the addition of a considerable excess of concentrated ammonium carbonate solution (100 gms.  $(\text{NH}_4)_2\text{CO}_3$ , 300 cc.  $\text{NH}_4\text{OH}$ , sp. gr. 0.96; after filtering 100 cc. of  $\text{NH}_4\text{OH}$ , sp. gr. 0.90, are added) will cause the complete precipitation of magnesium ammonium carbonate,  $\text{MgCO}_3(\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . The separation of magnesium from the alkalies may be effected in this way.

The magnesium ammonium carbonate is fairly soluble in water and the solubility increases rapidly with rise of temperature. Thus no precipitate is obtained upon the addition of ammonium carbonate to a dilute solution of magnesium salt containing ammonium chloride. (Note difference from barium, strontium and calcium).

4. **Sodium Phosphate** is the characteristic reagent for magnesium. It produces in solutions containing ammonium chloride, and in the presence of ammonia, a white crystalline precipitate (orthorhombic, hemimorphous) of magnesium-ammonium phosphate,\*



Rubbing the sides of the beaker with a glass rod hastens the formation of the precipitate. From very dilute solutions the precipitate separates only after standing some time.

#### REACTIONS IN THE DRY WAY.

All magnesium salts are more or less changed on heating in the air, leaving behind the oxide or an insoluble basic salt. On char-

\* Magnesium ammonium phosphate crystallizes with six molecules of water.

coal with sodium carbonate before the blowpipe, magnesium compounds are changed to white magnesium oxide, which is strongly luminous when hot. Calcium, strontium, and aluminium compounds behave the same way. The magnesium salts are non-volatile, do not color the flame, and give no flame spectrum, but do give a characteristic spark spectrum.

DETECTION AND SEPARATION OF MAGNESIUM AND THE ALKALIES IN THE PRESENCE OF ONE ANOTHER.

These metals are assumed to be present in the form of chlorides.

Ammonium is tested for, first of all, by heating a small part of the substance with caustic soda solution. The rest of the substance is used in testing for magnesium, potassium, and sodium. It is divided into two parts, one being used in the test for magnesium and the other for sodium and potassium.

In order to test for magnesium, the substance is dissolved in as little water as possible; or, in case we have a solution, it is evaporated to dryness and then dissolved in a little water. To the solution, ammonium chloride is added (if not already known to be present), and then ammonia. In case ammonia produces a precipitate of  $\text{Mg}(\text{OH})_2$ , enough more ammonium chloride must be added to dissolve it. Sodium phosphate solution is now added, and the sides of the beaker rubbed with a glass rod. If there is magnesium enough present to amount to a few tenths of a milligram per 100 cc. of the solution, a precipitate of magnesium-ammonium phosphate will surely appear within two or three minutes. If no precipitate is formed, the beaker is set aside in order to see if small crystals will be deposited on the bottom and rubbed sides after twelve hours. These crystals are more apparent on pouring off the solution. If the crystals appear on standing, then traces of magnesium are present.

Before testing for sodium and potassium the solution must be freed from magnesium; and, as ammonium salts are usually present, it is necessary to evaporate to dryness and drive them off by gentle ignition. Heating to redness must be avoided, in order to prevent loss of sodium and potassium by volatilization. The residue from ignition is dissolved in a little water (it is not necessary to obtain a perfectly clear solution, as a little basic salt of magnesium usually remains undissolved), and barium hydroxide solution is added until the solution is strongly alkaline, when it is boiled and



the magnesium hydroxide filtered off. This operation must be carried on in a platinum or good porcelain dish, never in glass, lest some alkali from the glass get into the solution. The filtrate, which is now free from magnesium, is cautiously acidified with hydrochloric acid, freed from the excess of barium hydrate by precipitation with ammonia and ammonium carbonate at the boiling temperature and filtering off the crystalline barium carbonate. The filtrate is now evaporated to dryness, the ammonium salts are driven off by ignition, and the residue is dissolved in a little water. In order to be sure that the barium is completely removed from the solution, it is treated again with ammonia and ammonium carbonate, filtered, evaporated to dryness, and the ammonium salts driven off as before. The residue is again dissolved in a little water, and the small amount of black carbonaceous matter (due to carbonization of a small amount of pyridine bases in the ammonia) is filtered off. A small part of the solution is now tested for potassium on a watch-glass by means of chloroplatinic acid, a yellow crystalline precipitate showing the presence of potassium. The larger part of the solution is used in testing for sodium by means of the flame reaction, and by potassium pyroantimonate. A white crystalline precipitate with the latter reagent shows the presence of sodium.

#### GROUP IV. ALKALINE EARTHS

##### CALCIUM, STRONTIUM, BARIUM,

##### GENERAL CHARACTERISTIC REACTIONS.

The metals of the alkaline-earth group are bivalent and heavier than water, which they decompose slowly at ordinary temperatures, with evolution of hydrogen and formation of difficultly soluble hydroxides of strongly alkaline reaction. The salts are mostly colorless and insoluble in water. The halogen compounds, nitrates, nitrites, and acetates are soluble in water. The carbonates are insoluble in water and are decomposed on ignition into carbon dioxide, and white infusible, strongly luminous metallic oxide:



Strontium carbonate is less readily decomposed than calcium carbonate, and barium carbonate loses its carbon dioxide only when heated to a white heat; its oxide is not very luminous.

The sulphates and oxalates are very difficultly soluble. The

sulphate of barium is the most insoluble and calcium sulphate the most soluble; of the oxalates, the calcium salt is the most insoluble. The solubility of the strontium salt is always midway between that of the corresponding calcium and barium salt, for the atomic weight of strontium, of which the solubility is a function, lies midway between the atomic weights of barium and calcium. The halogen salts are volatile and impart a characteristic color to the flame.

The metals of this group form oxides of the general type  $RO$ , and peroxides corresponding to the formula  $RO_2$ . The latter, on treatment with acids, give hydrogen peroxide and salts corresponding to the oxide  $RO$ :  $RO_2 + 2HCl = H_2O_2 + RCl_2$ .

### CALCIUM, Ca. At. Wt. 40.07.

Sp. Gr. 1.58. M. Pt.  $780^\circ C$ .

*Occurrence.*—Calcium is widely distributed in nature. It is found in enormous deposits in all stratified formations as carbonate (limestone, marble, chalk), often rich in petrification. The carbonate,  $CaCO_3$ , is dimorphous, crystallizing in rhombohedrons as calcite and in the orthorhombic system as aragonite. Calcium also occurs in large masses as sulphate, partly as monoclinic crystallizing gypsum,  $CaSO_4 \cdot 2H_2O$ , and partly as the anhydrous anhydrite,  $CaSO_4$ , which crystallizes in the orthorhombic system. Calcium also occurs as fluoride, fluorite,  $CaF_2$ , which crystallizes in the isometric system, with perfect octahedral cleavage; as apatite,  $3Ca_3P_2O_8 \cdot Ca\overset{Cl}{F}$ , which belongs to the hexagonal system; and, finally, in innumerable silicates, such as the monoclinic wollastonite,  $CaSiO_3$ , and the triclinic anorthite,  $CaAl_2Si_2O_8$ . The calcium minerals are the chief representatives of several important isomorphous groups:

#### *Calcite Group, Rhombohedral. Aragonite Group, Orthorhombic.*

Calcite,	$CaCO_3$	Aragonite,	$CaCO_3$
Magnesite,	$MgCO_3$	Strontianite,	$SrCO_3$
Dolomite,	$Ca \left. \begin{array}{l} \\ \end{array} \right\} CO_3$	Witherite,	$BaCO_3$
	$Mg \left. \begin{array}{l} \\ \end{array} \right\} CO_3$	Cerussite,	$PbCO_3$
Siderite,	$FeCO_3$		
Smithsonite,	$ZnCO_3$		
Rhodochrosite,	$MnCO_3$		

#### *Anhydrite Group, Orthorhombic.*

Anhydrite,	$CaSO_4$
Celestite,	$SrSO_4$
Barite,	$BaSO_4$
Anglesite,	$PbSO_4$

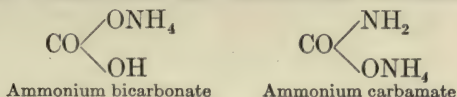
#### *Apatite Group, Hexagonal.*

Apatite,	$3Ca_3P_2O_8 + Ca(ClF)$
Pyromorphite,	$3Pb_3P_2O_8 + PbCl_2$
Mimetite,	$3Pb_3As_2O_8 + PbCl_2$
Vanadinite,	$3Pb_3V_2O_8 + PbCl_2$

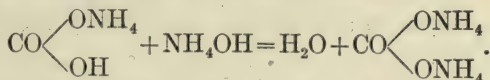
## REACTIONS IN THE WET WAY.

1. **Ammonia**, in case it is free from carbonate, produces no precipitate with calcium salts; on standing in the air, however, carbonic acid is absorbed and a turbidity of calcium carbonate results.

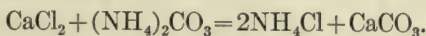
2. **Ammonium Carbonate**.—The commercial salt is a mixture of ammonium bicarbonate and ammonium carbamate:\*



We therefore add ammonia to the reagent, whereby the ammonium bicarbonate is changed to normal carbonate:



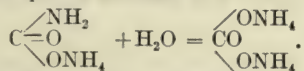
The commercial salt and ammonia produce in solutions containing calcium salts, at first a voluminous, flocky precipitate, which on standing gradually becomes crystalline, the change taking place more quickly on heating:



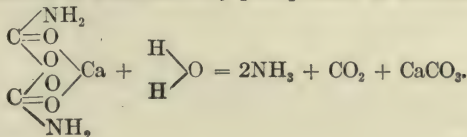
This reaction is noticeably reversible. Consequently, an excess of the precipitant should be added, and the solution boiled only long enough to cause the precipitate to become crystalline. In the presence of considerable ammonium chloride, and with only a small amount of ammonium carbonate, the precipitate often fails to form.

3. **Ammonium Oxalate** produces in neutral or alkaline solutions a precipitate of calcium oxalate, which when formed from

\* The ammonium carbamate is changed completely to ammonium carbonate on warming the aqueous solution to 60° C.:

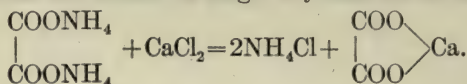


Ammonium carbamate produces no precipitate with calcium salts in the cold, because calcium carbamate is soluble. If, however, the solution be heated, the calcium is quantitatively precipitated as carbonate:

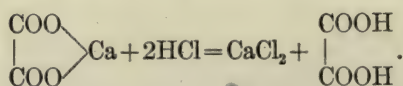




cold solutions is composed of extremely fine crystals, hard to filter, while from hot solutions larger crystals are formed:

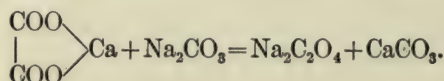


Calcium oxalate is practically insoluble in water and acetic acid, but dissolves readily in mineral acids:

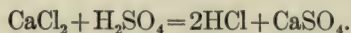


Ammonia precipitates from such a solution calcium oxalate again, the excess of mineral acid, as well as the oxalic acid which was set free, being changed to ammonium salt, causing the formation of calcium oxalate.

Calcium oxalate on being boiled with sodium carbonate solution is easily changed to carbonate:



4. **Sulphuric Acid** produces a precipitate only in concentrated solutions:



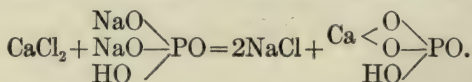
100 parts water dissolve at 40° C. 0.214 gm.  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ .

If alcohol is added to an aqueous solution of calcium sulphate, all of the calcium salt will be precipitated.

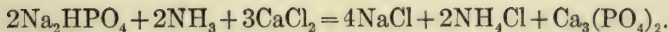
Calcium sulphate dissolves in hot dilute hydrochloric acid, and also in concentrated ammonium sulphate solution, forming  $[\text{Ca}(\text{SO}_4)_2](\text{NH}_4)_2$ , which is decomposed by water.

5. **Calcium Sulphate** solution produces no precipitation with calcium salts. (Note distinction from strontium and barium.)

6. **Sodium Phosphate** ( $\text{Na}_2\text{HPO}_4$ ) produces in neutral solutions a white, flocculent precipitate of calcium hydrogen phosphate:



If ammonia is added to the solution at the same time, tertiary calcium phosphate will be precipitated:



Both of these phosphates of calcium are soluble in mineral acids, or even acetic acid. From such solutions ammonia always precipitates the tertiary salt.

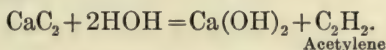
7. **Chromates of the Alkalies** do not precipitate calcium salts from dilute solution. (Note distinction from barium.)

8. **Absolute Alcohol**, or a mixture of equal parts of absolute alcohol and ether, dissolves both the nitrate and chloride of calcium.

*All deliquescent salts, with the exception of potassium carbonate, dissolve in absolute alcohol.* All other salts are, as a rule, insoluble, or very difficultly soluble, in absolute alcohol. An exception to this rule is found in the case of mercuric chloride, which is not deliquescent, and is much more readily soluble in alcohol than it is in water.

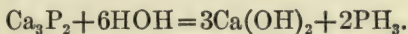
9. **Water** decomposes the carbide, phosphide, and nitride of calcium at the ordinary temperature, as follows:

(a) the carbide:



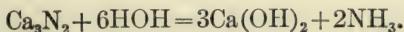
Acetylene is evolved by the reaction, a gas with a peculiar smell.\* If this gas is conducted into an ammoniacal copper solution, it rapidly produces a red precipitate of copper acetylide. The latter compound is harmless while it is moist; but in the dry state it can be readily exploded by a blow, by rubbing, or by simply warming.

(b) The phosphide:



The garlic-smelling phosphine gas which is evolved is spontaneously combustible, because it always contains a small amount of the spontaneously-combustible, liquid phosphuretted hydrogen ( $\text{P}_2\text{H}_4$ ).

(c) The nitride:



#### REACTIONS IN THE DRY WAY.

Calcium compounds, on being heated with sodium carbonate before the blowpipe, are changed to the white infusible oxide, which glows brightly when hot.

The volatile calcium compounds color the non-luminous gas flame brick-red.

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\* Pure acetylene is odorless. Almost all calcium carbide contains a little calcium phosphide which evolves phosphine on treatment with water.

*Flame Spectrum.*—Orange-yellow double line ( $620.3 \mu\mu$ ,  $618.2 \mu\mu$ ) and a yellowish-green one ( $554.4 \mu\mu$ ,  $551.8 \mu\mu$ ); both of these lines belong to calcium oxide. If calcium chloride wet with hydrochloric acid is placed in the flame, a number of other lines are seen; in the orange-yellow  $646.6 \mu\mu$ ,  $606.9 \mu\mu$ ,  $604.5 \mu\mu$  and  $593.4 \mu\mu$ , in the yellow  $581.7 \mu\mu$  and  $572.0 \mu\mu$ , in the violet usually very hard to see,  $422.7 \mu\mu$ , (see spectroscopic chart, Frontispiece).

**STRONTIUM, Sr.** At. Wt. 87.63.

Sp. Gr. 2.5. Melts at red heat.

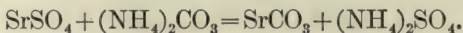
*Occurrence.*—Strontium occurs quite commonly with calcium, but usually in much smaller amounts. There are only a few true strontium minerals. The most important of these are: Strontianite,  $\text{SrCO}_3$ , orthorhombic, isomorphous with aragonite; and celestite,  $\text{SrSO}_4$ , orthorhombic, isomorphous with barite.

#### REACTIONS IN THE WET WAY.

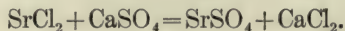
1. **Ammonia:** same as with calcium.
2. **Ammonium Carbonate:** same as with calcium.
3. **Ammonium Oxalate:** same as with calcium; but the strontium oxalate is somewhat soluble in acetic acid.
4. **Dilute Sulphuric Acid** produces a white precipitate of strontium sulphate:



Strontium sulphate is much less soluble in water than calcium sulphate (6900 parts of water at ordinary temperatures dissolve 1 part  $\text{SrSO}_4$ ), but much more soluble than barium sulphate. It is soluble in boiling hydrochloric acid, and insoluble in ammonium sulphate. By boiling with ammonium carbonate solution, the strontium sulphate is changed to carbonate:



5. **Calcium Sulphate** solution produces in neutral or weakly acid solutions, *after some time*, a precipitate of strontium sulphate:



6. **Chromates of the Alkalies** produce in dilute solutions no precipitate (thus differing from barium); but from concen-



trated solutions strontium chromate is precipitated. The precipitate is quite soluble in acetic acid.

**7. Absolute Alcohol.** The nitrate is not deliquescent, and does not dissolve in absolute alcohol. Although strontium chloride is deliquescent, the anhydrous salt dissolves scarcely at all in absolute alcohol, but the salt  $\text{SrCl}_2 + 6\text{H}_2\text{O}$  dissolves in alcohol (116.4 pts. of cold and 262 pts. of boiling absolute alcohol).

#### REACTIONS IN THE DRY WAY.

Heated on charcoal before the blowpipe the strontium compounds behave similarly to the calcium compounds.

The volatile strontium salts color the non-luminous gas-flame carmine red.

*Flame Spectrum.*—A number of lines in the red and orange yellow and one in the blue. No bands in the green. Red 686.3  $\mu\mu$ , 674.7  $\mu\mu$ , 662.8  $\mu\mu$ , 649.9  $\mu\mu$ ; orange-yellow 646.5  $\mu\mu$ , 635.1  $\mu\mu$ , 606.0  $\mu\mu$ ; blue 460.7  $\mu\mu$ .

**BARIUM, Ba.** At. Wt. 137.37.

Sp. Gr. about 4.0. M. Pt. 850° C.

*Occurrence.*—Like strontium, barium is almost always found associated with calcium, but only in small amounts. The most important barium minerals are: Witherite,  $\text{BaCO}_3$ , orthorhombic, isomorphous with aragonite; barite, or heavy spar,  $\text{BaSO}_4$ , orthorhombic, isomorphous with anhydrite; and the hydrous barium aluminium silicate, harmotome,  $\text{BaAl}_2\text{H}_2\text{Si}_5\text{O}_{15} + 4\text{H}_2\text{O}$ . Harmotome crystallizes in the monoclinic system, and belongs to the class of zeolites.

#### REACTIONS IN THE WET WAY.

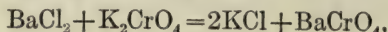
**1. Ammonia and Ammonium Carbonate:** same as with calcium and strontium.

**2. Ammonium Oxalate:** same as with calcium and strontium, except that the barium oxalate formed is much more soluble in water (1 part dissolves in 2590 parts of cold water), and is completely soluble in acetic acid on boiling.

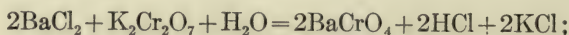
**3. Phosphates of the Alkalies:** same as with calcium.

**4. Chromates of the Alkalies** produce in neutral solutions of

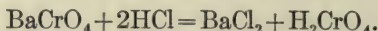
barium salts a yellow precipitate of barium chromate (thus differing from calcium and strontium),



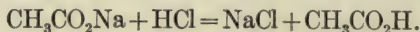
which is insoluble in water and acetic acid, but readily soluble in mineral acids; consequently barium solutions are not completely precipitated by a bichromate solution,



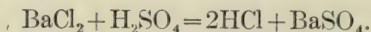
for the mineral acid which is set free dissolves half of the barium chromate:



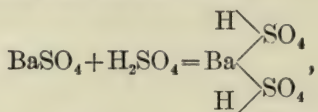
By addition of sodium acetate the solvent action of the mineral acid is diminished, so that the precipitation becomes quantitative:



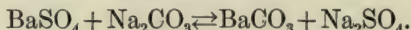
**5. Dilute Sulphuric Acid** produces, in even the most dilute solutions, a precipitate of barium sulphate:



The precipitate is practically insoluble in water (1 gm. dissolves in 436,700\* liters of water), but it is soluble in hot concentrated sulphuric acid, forming an acid sulphate,



which decomposes, on dilution with water, into barium sulphate and sulphuric acid. Barium sulphate is slightly soluble in boiling hydrochloric acid. If barium sulphate is boiled with a solution of sodium carbonate, it undergoes only a partial decomposition, because the reaction is reversible:



In order to make this decomposition quantitative, the barium sulphate must be boiled with the sodium carbonate solution, filtered, treated with a new portion of sodium carbonate solution, and the process repeated until the filtrate no longer gives a test for sulphate. The more concentrated the sodium carbonate

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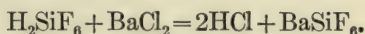
\* Fr. Kohlrausch and Fr. Rose, *Z. phys. Chem.* **12**, 241.

solution is, the more complete will be the decomposition. The highest degree of concentration will be reached by *fusion of the barium sulphate with anhydrous sodium carbonate*.

Consequently, in order to bring barium sulphate into solution, we proceed as follows: The substance is mixed with four times as much calcined sodium carbonate, and the mixture fused in a platinum crucible. The product of the fusion is treated with a *little* water, boiled until the mass is disintegrated, filtered, washed with a solution of sodium carbonate (until the filtrate no longer gives a test for sulphate), and then washed with water. The barium carbonate, which remains undissolved, can be readily brought into solution by means of dilute hydrochloric acid.

If the product of the fusion is treated with *considerable* water, the sodium sulphate formed reacts with the barium carbonate, forming barium sulphate again. In this case the residue insoluble in water will not dissolve in hydrochloric acid to a clear solution.

**6. Hydrofluosilicic Acid** produces a white, crystalline precipitate of barium silicofluoride:



In order to effect complete precipitation, the solution must stand some time. Barium silicofluoride is difficultly soluble in water and dilute acids, and insoluble in alcohol.

**7. Absolute Alcohol** dissolves neither the nitrate nor the chloride; neither of these salts is deliquescent.

**8. Concentrated Hydrochloric Acid and Nitric Acid** will precipitate from barium solutions the chloride and nitrate respectively.

#### REACTIONS IN THE DRY WAY.

Heated with sodium carbonate on charcoal before the blowpipe, the barium compounds, unlike calcium and strontium, do not give a brightly luminous mass, because the barium carbonate formed is not decomposed at this temperature into the infusible oxide and carbon dioxide, but merely sinters together somewhat. Volatile barium salts color the non-luminous gas-flame yellowish-green. The sulphate is only slightly volatile in the hottest flame, and in the ordinary gas-flame it shows scarcely any coloration. In order to obtain the coloration, it is best to change the sulphate



into chloride, by reducing a small particle on a platinum wire in the upper reducing flame to sulphide and adding a little hydrochloric acid by means of a capillary tube. The wire on then being brought into the flame will give the characteristic flame coloration.

*Flame Spectrum.*—A number of deep green lines, weaker lines in the orange-yellow part of the spectrum, and one blue line.

Orange-yellow (654.0  $\mu\mu$ , 629.8  $\mu\mu$ ), (624.0  $\mu\mu$ , 617.9  $\mu\mu$ , 610.9  $\mu\mu$ , 603.2  $\mu\mu$ ). Yellow 528.5, yellow triple line (576.9  $\mu\mu$ , 572  $\mu\mu$ , 564.8  $\mu\mu$ ). Green 553.5  $\mu\mu$ , 534.7  $\mu\mu$ , 524.3  $\mu\mu$ , 513.7  $\mu\mu$ , 500.0  $\mu\mu$ . Blue, 484.7  $\mu\mu$ .

### Separation of Calcium, Strontium, and Barium.

In the course of a systematic analysis these three metals are always obtained in the form of their insoluble carbonates, either by precipitation with ammonium carbonate or by fusion of the sulphate with sodium carbonate.

The carbonates are treated in a small porcelain dish with dilute nitric acid (barium nitrate is insoluble in concentrated nitric acid), until all effervescence has ceased, and the contents of the dish cautiously evaporated to dryness (keeping the dish in constant motion); the residue is heated until all moisture and nitric acid have been expelled. The nitrates must not be heated hot enough to decompose them into oxides. A small part of the residue is dissolved in as little water as possible, and treated with calcium sulphate solution.

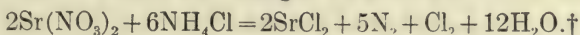
If *no precipitate* is formed, then only *calcium* can be present.

If a precipitate forms *only after standing some time*, then *barium is absent*. If a precipitate is formed *immediately*, then *barium* is present and *calcium* and *strontium* may be present. In both of the last two cases the nitrates must be examined for calcium, and in the last case for strontium also. To effect this, the absolutely dry nitrates are treated with a small quantity of absolute alcohol, stirred with a glass rod, and the alcoholic solution, which may contain calcium nitrate, is poured through a filter (previously moistened with alcohol) into a small porcelain crucible. The contents of the crucible are now evaporated to dryness, and any calcium salt adhering is removed by rubbing the inside of the crucible with a piece of filter-paper, which must itself be free from calcium.

The filter-paper is fastened to a fine platinum wire, burned to an ash, moistened with hydrochloric acid (by means of a capillary tube), and introduced into the non-luminous flame of the burner. A *brick-red* coloration shows *calcium*.

If a considerable residue remains after the evaporation of the alcohol, it can, of course, be tested for calcium without using the filter-paper. A portion of the residue should in this case be dissolved in water, and tested for calcium by means of ammonium oxalate. A white precipitate, insoluble in acetic acid, shows the presence of calcium.

In order to detect *strontium*, the original residue of nitrates is washed with absolute alcohol (until the filtrate no longer gives a test for calcium with sulphuric acid), dried, mixed with an excess of ammonium chloride, and heated until vapors of ammonium salts are no longer given off. By this operation the nitrates of strontium and barium are changed to chlorides.\*



The chlorides thus obtained are treated, as above, with a little absolute alcohol, and the alcoholic solution is evaporated and tested for strontium by means of the flame. A *carmine-red* color shows *strontium*.

The residue insoluble in alcohol, which should be barium chloride, is washed with absolute alcohol in order to remove all the strontium chloride, and the residue is, in this case also, tested with the flame. A *yellowish-green* color shows the presence of *barium*.

*Traces of alkalis* and *alkaline earths* are recognized best by means of the spectroscope. We will, therefore, at this place give a brief description of spectrum analysis.

### Spectrum Analysis (Bunsen and Kirchhoff, 1865).

If a ray of white light is passed through a glass prism, not only is the direction of the ray changed, but the white light is decomposed into colors; it suffers dispersion. It will be found that the

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\* It is also easy to convert the nitrates into chlorides by repeated evaporation with hydrochloric acid.

† The following reaction also takes place to some extent:



red rays are deflected least, while the violet rays are most deflected.

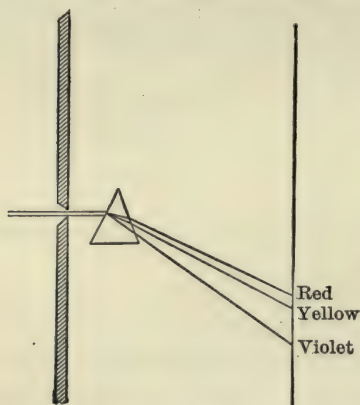


FIG. 5.

The picture obtained—the spectrum—if projected on a screen (Fig. 5), does not show the colors sharply separated, but merging into one another. Such a spectrum is called a continuous, or uninterrupted, spectrum. *Every glowing solid or liquid body emits white light; the spectra obtained in all such cases will be continuous ones.* Glowing vapors and gases behave quite differently. They do not emit white light, but light composed of

certain definite rays, which are characteristic for each gas and for each vapor. The light emitted from glowing vapors or gases, when decomposed by the prism, yields on the screen an interrupted spectrum. If the light is passed through a fine slit before reaching the prism, the spectrum will be found to consist of a greater or less

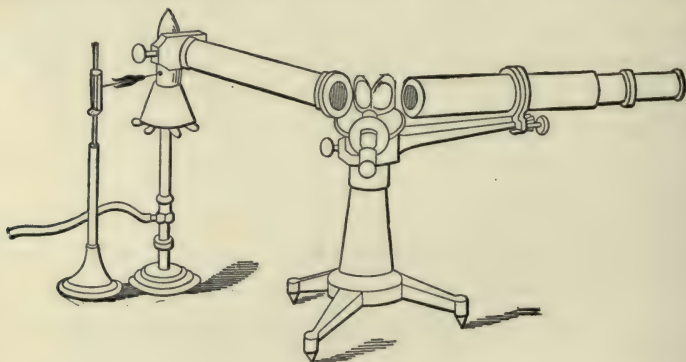


FIG. 6.

number of colored lines which always appear in the same place with any given substance, provided the prism or its position is not changed. In order to determine the exact position of these lines, we make use of the spectroscope of Bunsen and Kirchhoff (Fig. 6). Fig. 7 shows a cross-section of the apparatus.

The substance to be examined is placed in the loop of a platinum



wire and introduced at *A* into the non-luminous gas-flame, by means of which it is volatilized.\* The rays of light pass through the slit into the tube *Sp*, reach the prism, by which the rays are refracted into the telescope *C* (the collimator) and are observed at *D*. Upon a glass plate at the end of the tube *Sk* is a transparent scale, which is illuminated by a small flame at *B*. This tube is so inclined toward

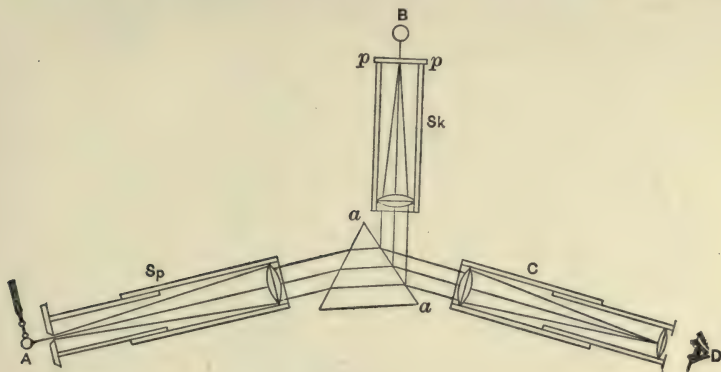


FIG. 7.

the face *aa* of the prism that the rays of light from this tube are totally reflected into the tube *C*, and reach the eye of the observer; thus the rays from the substance appear at a certain position on the scale. As, however, the position of the lines depends upon the dispersive power of the prism, and upon its angle of refraction, it is clear that the position of the lines will be somewhat different in different spectroscopes. As every ray has a definite wave length, it is better to give the wave lengths of the rays which appear, rather than their position on the scale.

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\* The spectra thus obtained are very beautiful but usually of short duration. More permanent spectra may be obtained with the aid of the Beckmann burner, Fig. 8 (cf. *Z. phys. Chem.* **11**, 472). From one-half to 1 cc. of the salt solution to be tested is placed in the glass vessel *G*, the gas is lighted, and a good blast of air introduced at *a*. By means of the air current, a little of the solution is carried mechanically over into the burner in the form of spray, and thus the salt reaches the non-luminous flame. In this way it is possible to get a fairly permanent spectrum by the use of only a few milligrams of substance. There is then plenty of time to make the measurements without having to stop and replenish the sample.

Wave lengths are expressed in millionths of a millimeter called micromillimeters and designated as  $\mu\mu$ .

The following values for the wave-lengths of the various lines in the spectrum are taken from the most accurate measurements:

Red rubidium line.....	Rb $\delta$	=795.0 $\mu\mu$
“ “ “ .....	Rb $\gamma$	=781.1 “
“ potassium double line.....	K $\alpha$	{ =766.9 “ =766.5 “
“ lithium line.....	Li $\alpha$	
“ cadmium line *.....	Cd $\gamma$	=643.9 “
Orange-yellow lithium line.....	Li $\beta$	=610.3 “
Yellow sodium (middle of the double line).....	Na	=589.3 “
Green calcium line.....	Ca $\beta$	=554.4 “
“ thallium line.....	Tl	=535.0 “
“ cadmium line*.....	Cd $\alpha$	=508.6 “
Blue “ “ “ *.....	Cd $\beta$	=480.0 “
“ “ “ “ *.....	Cd $\gamma$	=467.8 “
“ strontium line.....	Sr $\delta$	=460.7 “
“ caesium line.....	Cs $\beta$	=459.3 “
“ “ “ “ .....	Cs $\alpha$	=455.3 “
Blue-violet indium line.....	In $\alpha$	=451.1 “
Violet rubidium line.....	Rb $\beta$	=421.2 “
“ .....	In $\beta$	=420.2 “
“ indium line.....		=410.1 “
“ potassium line.....	K $\beta$	=404.4 “
H (Frauenhofer C line).....		=396.8 “

Let us assume that the foregoing lines were observed at the following positions on the scale: K $\alpha$  at 17, K $\beta$  at 154, Li $\alpha$  at 32, Na at 50, Tl at 68, Sr $\delta$  at 101, In $\alpha$  at 111, and In $\beta$  at 149.

If now, upon a rectangular system of coordinates, we plot the wave lengths as ordinates and the corresponding scale divisions as abscissas, and connect the points of intersection, we shall get a curve\* which expresses the relation between the wave lengths and the corresponding divisions on the scale (Fig. 9).

\* The cadmium lines can only be seen distinctly in spark spectra.

\* The curve is ordinarily only for wave lengths lying between 800–400  $\mu\mu$  because only these light rays are visible to the eye. The rays of shorter wave length than 400  $\mu\mu$  are called *ultra-violet rays* and those longer than 800  $\mu\mu$  are known as *ultra-red rays*. The former can be detected by their action upon photographic plates, and the latter by their thermic effect or by their action upon specially-prepared photographic plates.





The scale divisions increase in their value as the wave lengths diminish, so that we subtract the 30.17 from 589.3.

### Measuring the Lines and Bands of the Spectrum.

The correctness of a curve of wave-lengths, prepared as just described, depends upon the accuracy with which the observed lines or bands are measured. To insure accuracy, all the better forms of apparatus are provided with cross-hairs in the ocular, and the cross must each time be made to cover a definite part of the line to be measured. The choice of such position depends upon the construction of the slit at the end of the spectroscope. If the apparatus is provided with an unsymmetrical slit, *i.e.*, one of which only one side is movable while the other remains in a fixed position, then the reading should be made with the cross-hairs

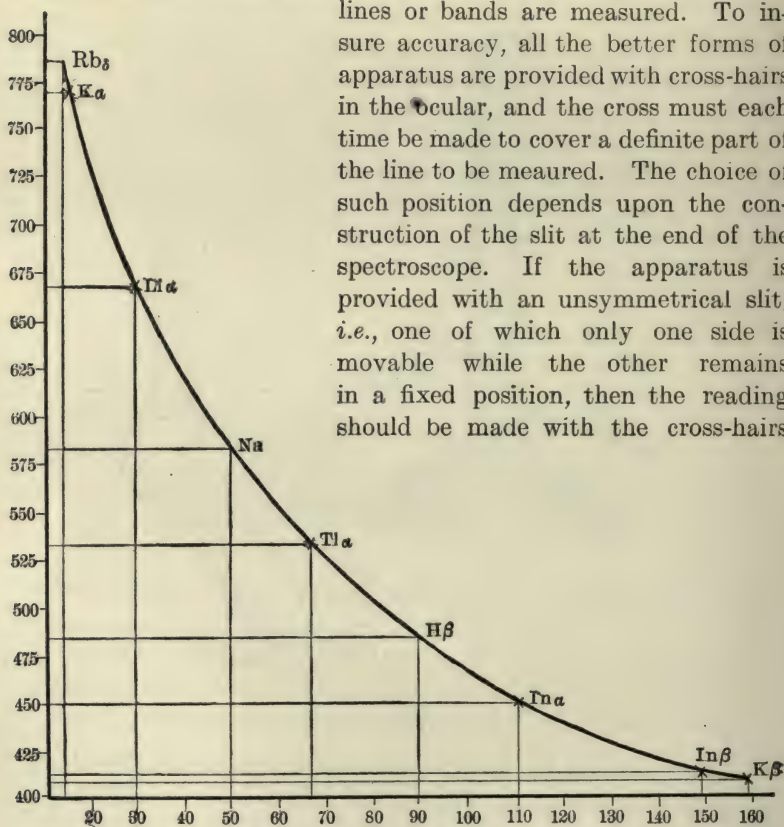


FIG. 9.

coinciding with the edge of the band on the immovable side of the slit. Such a position is shown in Fig. 10, in which it is assumed that the right-hand side of the slit is immovable.

In the case of a symmetrical slit, *i.e.*, one in which both

sides of the slit open and close symmetrically, the cross-hairs must be made to meet in the center of the line to be measured (Fig. 11).

The measurements can be made more readily and more accurately by the aid of Hilger's Wave Length Spectroscope (Fig. 12). In this apparatus the telescope and collimator are both fixed in position, but the prism can be rotated by means of a cylinder upon which is engraved a very exact wave-length curve

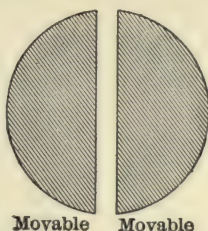
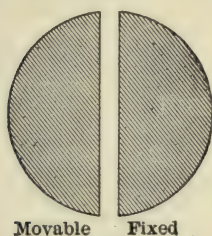


FIG. 10. Position with unsymmetrical slit.



FIG. 11. Position with symmetrical slit.

(Fig. 13). The pointer of the cylinder gives the desired wavelength with an accuracy of  $\pm 0.2 \mu\mu$ .

For the rapid adjustment of the apparatus, the ocular shown in Fig. 14 is convenient. In this ocular there is a very fine, polished steel point beneath the cross-hairs; it is lighted from the outside by means of a small mirror so that it is seen very distinctly. This point is made to coincide with the desired edge, or the middle of the line, and then only the final adjustment is made with the cross-hairs.

It is not possible to volatilize all substances in the gas-flame. These non-volatile bodies will not give any flame spectra, but by means of the electric spark they will be volatilized enough to give

spark spectra. As the determination of their spark spectra furnishes the only method by which the purity of many substances

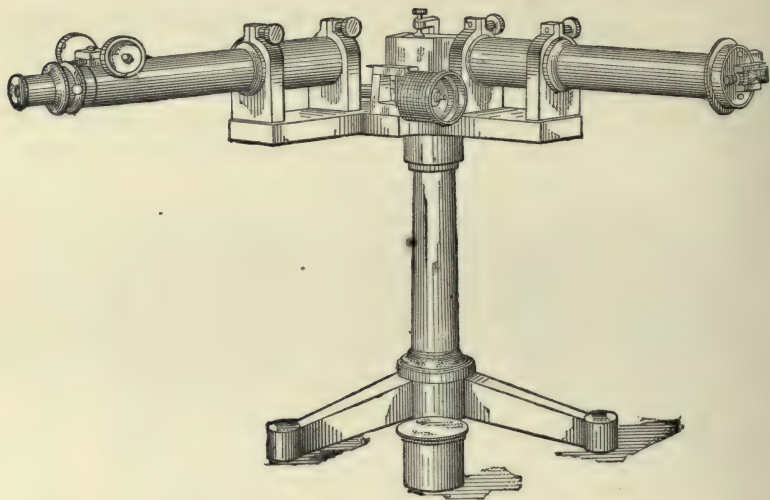


FIG. 12.

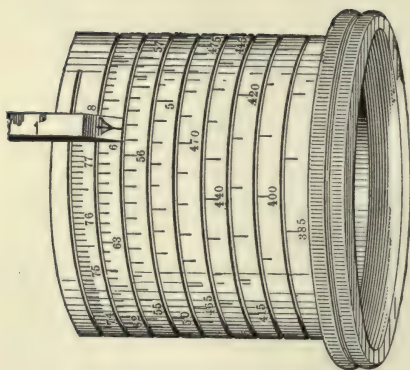


FIG. 13. Cylinder (enlarged).

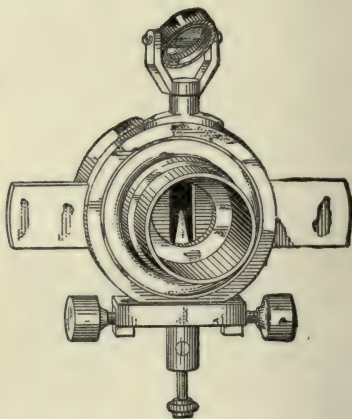


FIG. 14. Ocular with steel point and mirror.

may be tested, we will briefly outline the methods for the production of spark spectra:

The apparatus invented by Bunsen consists of two platinum



wires, which are each attached at one end to conical pieces of charcoal. The latter are soaked with a solution of the substance to be tested. The two carbon points are now placed opposite to one another, quite near together; and the other ends of the platinum wires are connected with an induction coil, which causes sparks to pass between the two carbon points, volatilizing some of the salt. If now the sparks are viewed through a spectroscope, a large number of lines will be seen, of which only a part are pro-

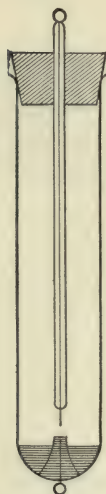


FIG. 15.

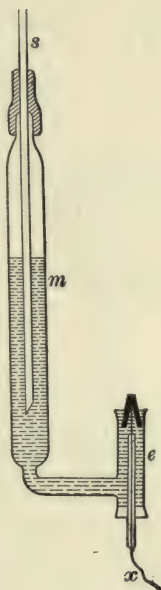


FIG. 16.

duced by the substance itself. Some of the lines are caused by the carbon points and some by the air. In order to determine which lines are caused by the substance that is being tested, the experiment is first performed without using any of the substance, and the spectrum thus obtained is either drawn or photographed. The experiment is then performed with some of the salt impregnated in the carbon points and the new lines in the spectrum will be caused by the substance.

Spark spectra can be more conveniently produced by means

of the so-called "fulgurator" of Delachanel and Mermet, as shown in Fig. 15. The salt solution is in a test-tube, so that the slit of the spectroscope cannot be contaminated with the spattered particles of the salt.

The small apparatus of H. Dennis, Fig. 16, is also very convenient for producing spark spectra. The platinum wire  $x$  is fused in a glass tube and ends in a point of Ceylon graphite, which extends up out of the arm  $e$  of the apparatus. The upper pole is not shown in the illustration.

In order to fill the tube  $m$  with the salt solution of the substance to be tested,  $s$  is taken away, and the apparatus is inclined to the left. The solution is poured in at the upper end of  $m$ , when

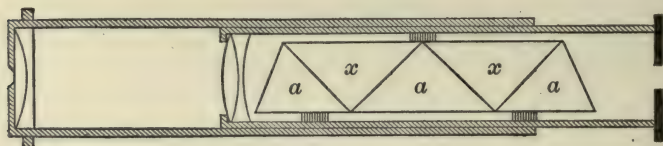


FIG. 17.

$s$  is again introduced and shoved down until it reaches nearly to the bottom. The apparatus is now placed in a vertical position, whereby the liquid in  $e$  rises until it is level with the lower end of  $s$ . On raising  $s$  the liquid will rise up to the upper edge of  $e$ . By means of electric sparks from the carbon point, enough of the liquid is evaporated to give the desired spectrum. Care should be taken to prevent any spattering of the substance into the slit of the spectroscope.

In order to examine the spectra of permanent gases, small Geissler tubes are used, which are filled with the gas to be examined. Besides flame spectra and spark spectra, there remain absorption spectra to be mentioned. If white light is passed through a colored solution or gas, certain rays are absorbed by the liquid, so that if the light is now examined in the spectroscope, these rays will be found to be lacking. We see a bright spectrum broken by black bands (absorption bands) which are characteristic for different substances. Thus solutions of permanganic acid, neodmium, praseodymium, erbium, and many other

substances give characteristic absorption spectra. These absorption spectra are often obtained from colorless solutions.

It is to be noted that an absorption spectrum is often of quite different appearance according to whether the solution is dilute or concentrated. In measuring absorption bands the solution should be diluted with solvent until the band appears in the form of as fine a line as possible at the intersection of the cross-hairs, and further dilution should cause the disappearance of the band.

The same end is easily attained if, as R. Philip has suggested, the concentrated solution is placed in a test-tube and covered

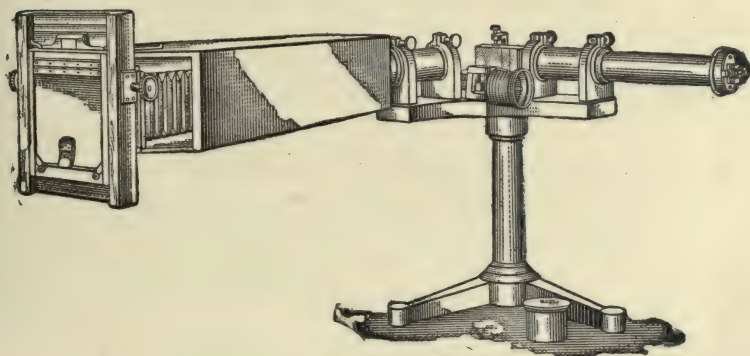


FIG. 18.

with more of the solvent. The lowest layer then gives the spectrum of the concentrated solution and it becomes more and more dilute in the upper portions.

In order to obtain any of the above spectra sharply defined, it is necessary to have the spectroscope properly adjusted, *i. e.*, the rays must come parallel from the collimator tube into the telescope. The telescope is removed and adjusted for parallel rays by focusing it upon some distant object. It is then replaced, the prism removed, and the collimator tube brought exactly opposite the telescope, so that the slit of the former can be observed by the latter. The collimator tube must be lengthened or shortened until the picture of the slit is sharply defined. The prism is now



replaced and the scale tube adjusted until the scale also can be seen clearly defined. The instrument is now ready for use.

The direct-vision pocket spectroscope, with an arrangement of prisms as shown in Fig. 17, is very convenient for ordinary use.

If it is desired to photograph a spectrum, the telescope tube is replaced by a camera as shown in Fig. 18. Such an apparatus is called the *spectrograph*. With glass prism and glass objective lens, the spectrum can be photographed to about 350  $\mu\mu$ . To make the ultraviolet part of the spectrum visible, the objective lens and the prism must be prepared of quartz and fluorspar, whereby it is possible to photograph light rays of about 200  $\mu\mu$ . For observing rays of still shorter wave length, fluorspar alone is requisite, as it absorbs the ultra violet rays to a less extent than quartz does.

To photograph the ultra red rays, specially prepared plates, as discovered and prepared by W. Abney, are necessary.

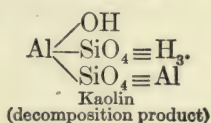
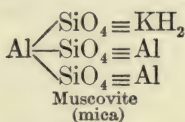
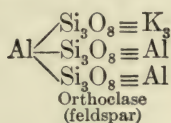
## GROUP III. AMMONIUM SULPHIDE GROUP.

ALUMINIUM, TITANIUM, CHROMIUM, IRON, URANIUM, ZINC, MANGANESE, NICKEL, COBALT. (BERYLLIUM, ZIRCONIUM, THORIUM, YTTRIUM, ERBIUM, CERIUM, LANTHANUM, NEODYMIUM, PRASEODYMIUM, NIOBIUM, TANTALUM.)

ALUMINIUM, Al. At. Wt. 27.1.

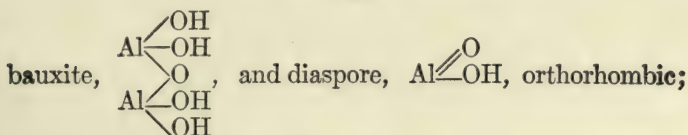
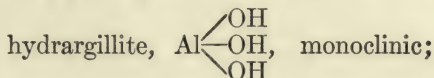
Sp. Gr. 2.56–2.67. M. Pt. = 657.3° C.

*Occurrence.*—Aluminium occurs very extensively in nature, principally in the form of silicates, of which the feldspars and micas with their decomposition products are important examples:



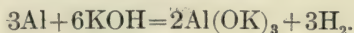
Impure kaolin is called clay.

Among the most important minerals which contain aluminium may be mentioned cryolite,  $\text{AlF}_6\text{Na}_3$ ; spinel,  $\text{Al}_2\text{O}_4\text{Mg}$ , or magnesium aluminate, which crystallizes in the regular system and is isomorphous with magnetite,  $\text{Fe}_2\text{O}_4\text{Fe}$ , and chromite,  $\text{Cr}_2\text{O}_4\text{Fe}$ ; alunite,  $\text{Al}_3\text{K}(\text{SO}_4)_2(\text{OH})_6$ ; aluminium hydroxide as

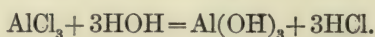


and corundum,  $\text{Al}_2\text{O}_3$  (ruby, sapphire, emery), which is hexagonal, rhombohedral, with a hardness of 9, and isomorphous with  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ .

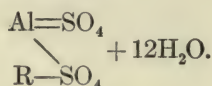
Aluminium is trivalent, of silver-white color, is only slightly affected by moist air, dissolves readily in hydrochloric acid, difficultly in sulphuric acid, and very difficultly in nitric acid, but readily in sodium or potassium hydroxide solution with evolution of hydrogen and formation of aluminates:



Aluminium forms only one oxide,  $\text{Al}_2\text{O}_3$ , and consequently only one series of salts. The salts are as a rule colorless, and those which are soluble in water show an acid reaction in aqueous solution, on account of their being hydrolyzed to a considerable extent. This explains the fact that on evaporating a solution of aluminium chloride in water we do not obtain aluminium chloride, but the insoluble oxide, or hydroxide:



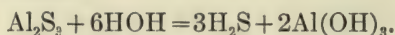
The property which aluminium possesses of forming alums is very characteristic. The alums are double salts of aluminium sulphate with the sulphates of potassium, caesium, rubidium, or ammonium, of the general formula



The alums crystallize in the regular system, usually in octahedrons, often combined with  $\infty \text{O} \infty$  and  $\infty \text{O}$ .

The common potassium alum is much less soluble in cold than in hot water. Thus 100 parts of water at  $15^\circ \text{C}$ . dissolve 10.7 parts of alum and 283 parts at  $100^\circ \text{C}$ .

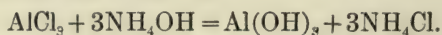
The sulphide of aluminium can be prepared only in the dry way. It is a pale-yellow substance, which is hydrolytically decomposed even by cold water into hydrogen sulphide and aluminium hydroxide:



Towards strong acids aluminium hydroxide plays the part of an alkali, while towards strong bases, on the other hand, it acts as an acid.

#### REACTIONS IN THE WET WAY.

1. **Ammonia** produces a gelatinous precipitate of aluminium hydroxide, which is somewhat soluble in water, but insoluble in the presence of ammonium salts:



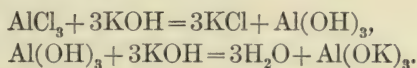
The property which the aluminium hydroxide shows of partly dissolving in water, is common to all *colloidal* substances. They can exist in an insoluble form as *hydrogel*, and in a soluble form as *hydrosol*.



On boiling a solution of the *hydrosol*, it can usually be changed into *hydrogel*, or the same change will take place on adding a salt to the solution. The hydrosol form of aluminium hydroxide cannot be converted into hydrogel by boiling, but it can be *by the addition of salts*,\* preferably ammonium salts. *If, therefore, we desire to precipitate aluminium from a solution by means of ammonia, we take care that a large excess of ammonium chloride is present.*

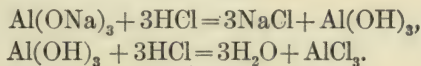
The freshly-precipitated aluminium hydroxide is readily soluble in dilute acids; but after standing some time in a salt solution, or after long boiling, it becomes more difficultly soluble, so that it is necessary to digest it with acid for a long time in order to bring it completely into solution.

2. **Potassium or Sodium Hydroxide** produces the same precipitate as ammonia which is, however, in this case soluble in excess of the reagent, forming an alkali aluminate:

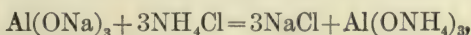


In this last reaction the aluminium hydroxide behaves as an acid.

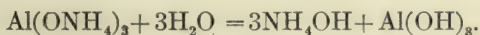
If we add dilute acid to a solution of an aluminate, there is formed at first a precipitate of aluminium hydroxide, which dissolves on further addition of acid:



The aluminates are also decomposed by ammonium salts, because ammonium aluminate suffers complete hydrolysis:



and

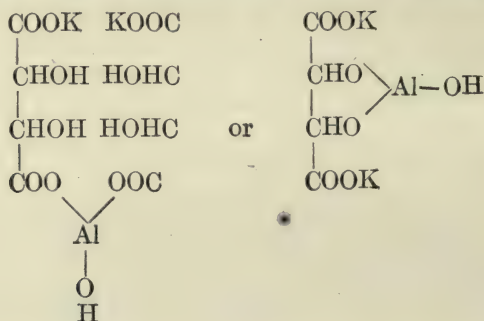


Aluminium hydroxide is soluble in neutral tartrates of the alkalis, so that in the presence of tartaric acid there will be no precipitation on the addition of ammonia. Consequently the aluminium cannot be present in the solution in the form of the simple alumin-

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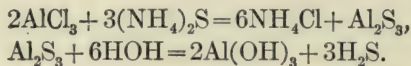
\* This principle is illustrated by the technical process of "salting out" colloidal dyes from their solutions.

ium cation, but as a complex negative ion. The aluminium is present then in the solution, not in the form of positive aluminium ions, but in a complex negative ion, perhaps of the salt:

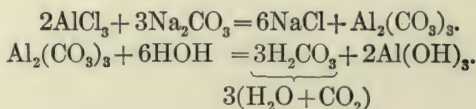


Many other organic hydroxy-acids and other hydroxy-compounds, such as malic and citric acids, sugars and starches, have the same effect of preventing the precipitation of aluminium hydroxide by ammonia.

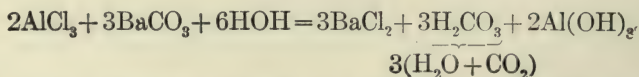
3. **Ammonium Sulphide** causes precipitation of the hydroxide, because the sulphide is completely hydrolyzed by water:



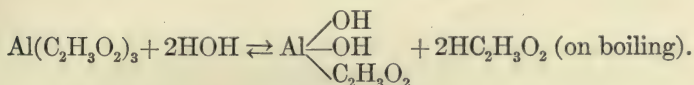
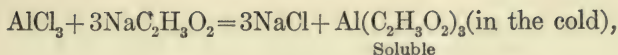
4. **Alkali Carbonates** precipitate aluminium hydroxide (hydrolysis):



5. **Barium Carbonate**, suspended in water and added to the solution of an aluminium salt, also precipitates the hydroxide:



6. **Alkali Acetates** produce no precipitation in cold neutral solutions, but, on boiling the solution, a very voluminous precipitate of basic *aluminium acetate* is formed:

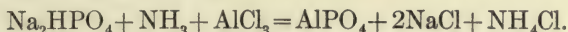


If the solution is allowed to cool, the basic aluminium acetate redissolves. The reaction is, therefore, a reversible one, and goes more completely from left to right according as we increase the amount of water and raise the temperature.

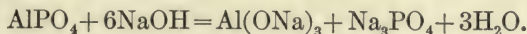
7. **Alkali Phosphates**, ( $\text{Na}_2\text{HPO}_4$ ), give a gelatinous precipitate of aluminium phosphate:



or, on addition of ammonia,

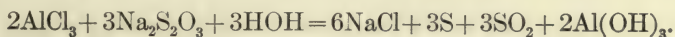


Aluminium phosphate is soluble in mineral acids, insoluble in acetic acid (differing from Ca, Sr, Ba, Mg), but readily soluble in sodium or potassium hydroxide solutions:



On boiling this alkaline solution (obtained in the last reaction) with ammonium chloride, a precipitate will be formed, consisting of a mixture of aluminium phosphate and aluminium hydroxide; while barium chloride, on the contrary, will precipitate barium phosphate from such a solution and leave the aluminate dissolved.

8. **Sodium Thiosulphate**,  $\text{Na}_2\text{S}_2\text{O}_3$ , completely precipitates the aluminium as hydroxide on boiling:



9. **Morin** in alcoholic solution shows a green fluorescence when brought in contact with only a trace of neutral aluminium salt- (This reaction is very sensitive.) Beryllium salts and salts of the rare earths do not give the test.

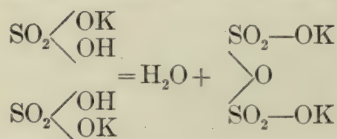
10. **Ether** precipitates white crystalline aluminium chloride,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  from a concentrated solution which is saturated with HCl gas. Aluminium may be separated from beryllium in this way.



DETECTION OF ALUMINIUM IN THE PRESENCE OF ORGANIC SUBSTANCES WHICH PREVENT THE PRECIPITATION BY THE ABOVE REAGENT.

The presence of tartaric acid or other non-volatile organic hydroxy-compounds prevents the precipitation with above reagents. To detect the presence of aluminium in such cases, the organic substance must be first destroyed. This is best accomplished as follows: Some sodium carbonate and a little potassium nitrate are added to the solution, which is then evaporated to dryness in a platinum dish, and the residue ignited, whereby the aluminium becomes aluminate, and the organic substance is destroyed with separation of carbon. If now the residue is treated with nitric acid \* and filtered, the aluminium goes into solution as nitrate and can be precipitated with any of the above reagents.

When strongly ignited, aluminium hydroxide loses water and forms the anhydride  $\text{Al}_2\text{O}_3$ , which is scarcely soluble at all in hydrochloric and nitric acids. In warm concentrated sulphuric acid, with a little water, it will dissolve after long digestion. The ignited aluminium oxide, as well as the natural corundum, is most readily brought into solution by fusion with potassium pyrosulphate. The fusion is accomplished in the following way: About twelve times as much commercial potassium acid sulphate as there is oxide to get into solution is first heated by itself in a large platinum crucible over a small flame. The acid potassium sulphate melts readily, at about  $300^\circ \text{C}$ ., gives off water (causing frothing), and becomes changed into potassium pyrosulphate:

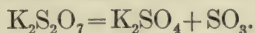


As soon as the frothing has ceased, the transformation into potas-

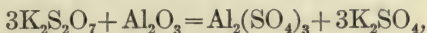
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\* If sufficient nitrate was present, the carbon will be completely burnt to  $\text{CO}_2$ , and the residue then often contains undecomposed nitrate or nitrite. It would, therefore, be unwise to treat the residue in the platinum dish with hydrochloric acid, as aqua regia would be formed and the platinum would be dissolved. Consequently the residue is treated with nitric acid (or with hydrochloric acid in a porcelain dish).

sium pyrosulphate is complete. The dry oxide is now added to the crucible, and the heating is continued until the melt begins to solidify (showing that a considerable amount of potassium sulphate, which melts much more difficultly than the pyrosulphate, has been formed), then the contents of the crucible are heated to a higher temperature and the heating is continued until the oxide has dissolved clear in the melt. By heating the pyrosulphate,  $\text{SO}_3$  is given off, which in the nascent state and at the high temperature is very active:

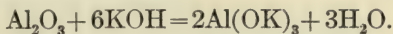


After the reaction is finished, the melt contains the aluminium as aluminium sulphate in the presence of potassium sulphate,



and both of these substances can be brought into solution by treating them with water.

The ignited aluminium oxide can also be brought into solution by fusion with caustic alkalies:



This last operation is usually carried on in a silver crucible, never in platinum, as the latter would be strongly attacked.

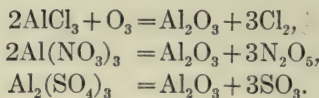
Native  $\text{Al}_2\text{O}_3$  (corundum, ruby, sapphire, emery) can be completely brought into solution by fusion with potassium pyrosulphate.

#### REACTIONS IN THE DRY WAY.

Aluminium compounds, on being heated with sodium carbonate on charcoal before the blowpipe give a white, infusible, brightly glowing oxide, which, when moistened with cobalt nitrate solution and again heated, becomes a blue infusible mass (Thénard's blue). This test is best accomplished by taking a small piece of filter-paper with the aluminium oxide on it, fastening it in a platinum spiral, moistening the paper with a little dilute nitric acid and warming, so that the substance is dissolved as much as possible, impregnated in the fibres of the filter-paper, and spread over a considerable surface. A few drops of dilute cobalt nitrate solution are now added, and the mass is strongly heated. Traces of aluminium can be recognized by the mass turning to a blue color. The presence of colored metallic oxides hinders the reaction.

Aluminium salts are not volatile, and do not color the flame. By ignition in the air, all aluminium salts, with the exception of the

phosphate and silicate, are decomposed, leaving behind the oxide:



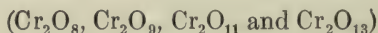
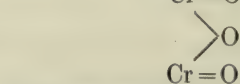
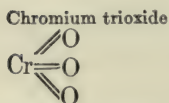
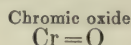
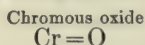
**CHROMIUM, Cr.** At. Wt. 52.0.

Sp. Gr. = 6.81. M. Pt. = 1515° C.

*Occurrence.*—Chromium occurs in nature as chromite,  $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ , isomorphous with spinel (see aluminium); as monoclinic crocoite,  $\text{PbCrO}_4$ ; and as laxmannite, a double compound of lead-copper phosphate and basic lead chromate,  $(\text{Pb,Cu})_3(\text{PO}_4)_2 \cdot \text{Pb}_3\text{O}(\text{CrO}_4)_2$ . Furthermore, it is found in small quantities in many silicates, such as muscovites, biotites, augites, etc., and consequently in their weathering products, as in many kaolins, bauxite, etc.

Metallic chromium is a white, crystalline powder.

With oxygen it forms the following oxides:

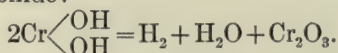


Chromium, therefore, exists in its compounds with a valence of either two, three, or six.

The oxides  $\text{CrO}$  and  $\text{Cr}_2\text{O}_3$  are basic anhydrides, and, on being dissolved in acids, yield the corresponding salts, the chromous and the chromic compounds. Chromium trioxide is the anhydride of the hypothetical chromic acid,  $\text{H}_2\text{CrO}_4$ , and forms chromates with bases. The chromium peroxides have never been obtained pure; salts of perchromic acid have been isolated and analyzed.\*

### I. CHROMOUS COMPOUNDS.

Chromous oxide is known only in the form of its hydroxide,  $\text{Cr}(\text{OH})_2$ , which, on being dried, loses hydrogen and water, leaving behind chromic oxide:




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\* See page 104.



Like chromous hydroxide, all chromous compounds are extremely unstable, being changed readily by contact with the air into chromic compounds.

Only the *halogen* compounds, the *phosphate*, *carbonate*, and *acetate*, are known in the dry state; the sulphate only in solution. The acetate,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$ , is a reddish-brown, crystalline substance, insoluble in water, but readily soluble in hydrochloric acid. This solution, as well as that of all chromous salts, absorbs oxygen with avidity, and is consequently used in gas analysis for the determination of oxygen in gas mixtures. Solutions of chromous compounds are obtained by the reduction of chromic compounds with nascent hydrogen (zinc and acid), out of contact with the air.

On account of the instability of these compounds the analytical chemist will rarely meet with them, so that we will pass over to the reactions of the chromic compounds.

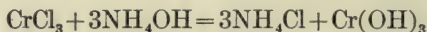
## II. CHROMIC COMPOUNDS.

All chromic compounds contain chromium as a trivalent element; they are colored either green or violet, and are soluble in water as a rule. The *oxide*, *hydroxide*, *phosphate*, *anhydrous chloride*, and the *sulphate*, after being strongly heated in a stream of carbon dioxide gas, are insoluble in water. Violet chromium chloride obtained in the dry way is insoluble in acids; it dissolves readily in water containing a trace of chromous chloride, or in the presence of stannous chloride (tin and hydrochloric acid). By dissolving the grayish-green chromic hydroxide in acids, green solutions are always obtained, which on long standing become greenish violet or violet but on boiling become green again. Chromic sulphate forms with sulphates of potassium, ammonium, caesium, or rubidium, the so-called chrome-alums, which crystallize in the regular system. These alums, like all other chromic salts, react acid in aqueous solution (hydrolysis).

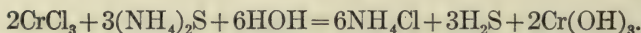
Chromic sulphide,  $\text{Cr}_2\text{S}_3$ , can only be obtained in the dry way. On being treated with water it is quantitatively decomposed into hydroxide and hydrogen sulphide.

## REACTIONS IN THE WET WAY.

1. **Ammonia** and **Ammonium Sulphide** produce a grayish-green, gelatinous precipitate of chromic hydroxide:

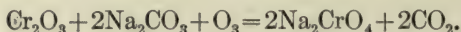


and



Chromic hydroxide is somewhat soluble in excess of ammonia, forming a violet-colored solution, particularly soluble when the ammonia is added to a *violet* solution of a chromic salt, in the presence of ammonium salts. This is caused by the formation of chromic-ammonium compounds, which, however, may be decomposed by boiling the solution until the excess of ammonia has been driven off, when the chromium is quantitatively precipitated as hydroxide. In order, then, to precipitate the chromium from a solution as hydroxide, it is necessary to precipitate at a boiling temperature, and to use as little ammonia as possible.

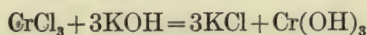
By ignition of chromic hydroxide, green chromic oxide is obtained, which after strong ignition is insoluble in acids. In order to bring it into solution, it must be fused with potassium pyrosulphate, as was described in the case of aluminium oxide; or with sodium carbonate and nitre in a platinum crucible, whereby it goes over into readily soluble sodium chromate:



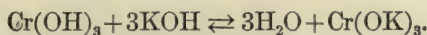
If the product of this last fusion is dissolved in water, acidified with hydrochloric acid, and boiled with alcohol, a green solution of chromic chloride will be obtained (page 104), from which the chromium can be precipitated as hydroxide with ammonia. On fusing with sodium carbonate and potassium nitrate in a platinum crucible, the latter will always be slightly attacked, so that a small amount of platinum will go into solution with the fused mass; it can be removed, after the treatment with hydrochloric acid, by passing hydrogen sulphide into the boiling solution, and filtering off the precipitated platinum sulphide.

2. **Potassium** and **Sodium Hydroxides** cause the same precipi-

tation as ammonia; only the precipitate is readily soluble in excess of the reagent, forming a green chromite:



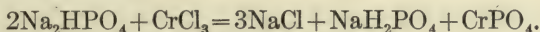
and



Chromic hydroxide behaves here as a weak acid. The reaction is reversible, the presence of considerable water causing the reaction to go from right to left, particularly at the boiling temperature. By boiling the dilute solution, complete hydrolysis takes place; the chromium is almost quantitatively precipitated as hydroxide (differing from aluminium).

3. **Alkali Carbonates, Barium Carbonate, Ammonium Sulphide, and Alkali Thiosulphates** precipitate chromic hydroxide, as with aluminium.

4. **Alkali Phosphates** give a greenish, amorphous precipitation of chromic phosphate:



Chromic phosphate is readily soluble in mineral acids and in cold acetic acid. On boiling the acetic acid solution, chromic phosphate separates out again.

5. **Alkali Acetates** produce in solutions of chromic salts no precipitation, neither in the cold nor on boiling. If, however, considerable amounts of aluminium and ferric salts are present at the same time, the chromium will be almost quantitatively precipitated with the iron and aluminium as basic acetate. In case, however, chromium predominates, only a part of the metals will be precipitated as basic salts; the filtrate will contain iron and aluminium with chromium. *In the presence of chromium, the basic acetate separation is always uncertain.*

6. **Hydrogen Sulphide** produces no precipitate in acid solutions of chromic salts.

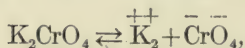
### III. CHROMATES.

Chromium trioxide,  $\text{CrO}_3$ , forms red orthorhombic needles, which dissolve readily in water to an orange-red solution. If we neutralize this solution with potassium hydroxide, it becomes yellow, and on evaporation we obtain the beautiful yellow-colored

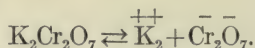


$K_2CrO_4$ , the potassium salt of chromic acid,  $H_2CrO_4$ . If the yellow solution of potassium chromate be acidified, and then allowed to crystallize, we obtain the beautiful orange-red prisms of triclinic potassium dichromate crystals,  $K_2Cr_2O_7$ .

The aqueous solution of potassium chromate,  $K_2CrO_4$ , contains colorless potassium ions and yellow  $CrO_4$  ions,



while the aqueous solution of potassium dichromate,  $K_2Cr_2O_7$ , contains, in the presence of the colorless potassium ions, the orange-red colored  $Cr_2O_7$  ions:



We are able, therefore, to determine from the color of a chromate solution the nature of the chromate ion which is present. Since, now, chromium trioxide dissolves in water with an orange-red color, we must assume that we have in the aqueous solution dichromic acid, or rather the dichromate ion, although the free acid itself has not yet been isolated. The normal chromic acid,  $H_2CrO_4$ , appears not to be capable of existence even in aqueous solution.

*Remark.*—Although we may judge as to the color of the ions from the color of the solution, and often predict what the color of the solid salt will be, yet, on the other hand, we cannot tell what the color of the solution will be from that of the salt itself. Yellow lead iodide dissolves in water to a colorless solution, and the yellow and red iodides of mercury, although only slightly soluble, also do not yield colored solutions.

*If the solution of a salt is colored, the salt itself will be colored; but the reverse is not always true.*

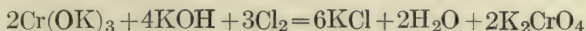
All chromates are insoluble in water, except those of the alkalis, calcium, strontium, and magnesium. All chromates dissolve in nitric acid, except fused lead chromate, which dissolves with difficulty.

#### *Formation of Chromates.*

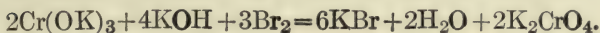
All chromium compounds may be readily oxidized to chromates. According to whether the compound is soluble in water or not, different methods are used to effect the oxidation.

*The oxidation of soluble chromates in alkaline solutions is effected:*

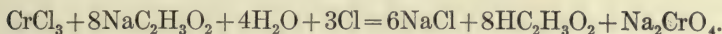
(a) By the halogens. If sodium or potassium hydroxide is added in excess to a solution of a chromic salt, and chlorine or bromine is conducted into the solution, the oxidation will be complete in a few minutes; the green chromite solution becomes a bright yellow:



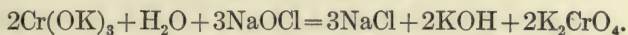
and



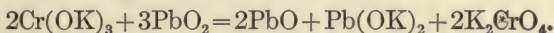
Chromic compounds may be also oxidized by halogens in the presence of sodium acetate, the reaction going extremely slowly in the cold, but very quickly on warming:



(b) By hypochlorites (sodium hypochlorite, chloride of lime, etc.):



(c) By lead peroxide. The alkaline solution is boiled with lead peroxide:

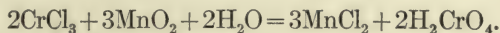


(d) By hydrogen peroxide,



the reaction taking place on warming.

(e) By freshly-precipitated manganese dioxide. The oxidation takes place on boiling the neutral or slightly acid solution:

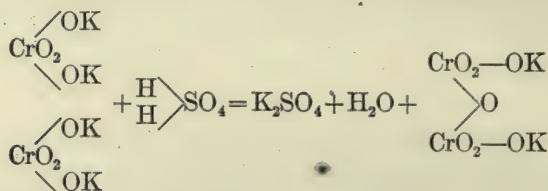


*Oxidation in acid solution* may be effected only by means of potassium chlorate in the presence of strong nitric acid.

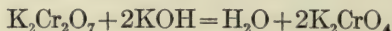
In the case of an insoluble chromium compound, such as strongly-ignited chromic oxide, or the mineral chromite, the oxidation is effected by means of fusion with sodium carbonate and either potassium nitrate or chlorate (cf. pp. 98, 108). The alkali chromates

thus obtained are of a deep-yellow color, and are readily soluble in water.

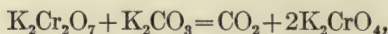
If acid is added to the solution of a normal chromate, the color is changed to orange in consequence of the formation of a dichromate:



Conversely, the dichromates of the alkalies are changed back into normal chromates by the addition of caustic alkali or alkali carbonates to the solution:



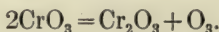
and



the solution becoming yellow again.

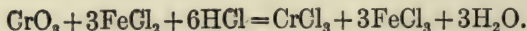
While alkaline solutions of chromic salts readily take on oxygen and become chromates, acid solutions of chromates, on the other hand, give off oxygen just as readily and become reduced to chromic salts again. *Chromic acid and chromates are strong oxidizing agents in acid solutions.*

The equation of oxidation, reduced to its simplest form, consists of chromium with a valence of six being reduced to chromium with a valence of three:

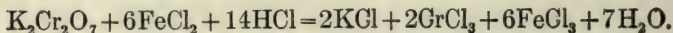


This decomposition, which takes place readily on igniting chromium trioxide, takes place just as readily in aqueous solution in the presence of readily oxidizable substances: thus ferrous salts are, even in the cold, immediately oxidized to ferric salts:

(a) By chromium trioxide:



(b) By potassium dichromate,

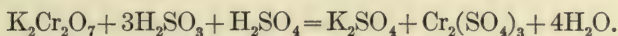




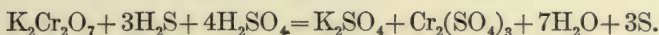
In this equation each chromium atom loses three valences and each iron atom gains one, so that one molecule of dichromate oxidizes six molecules of ferrous chloride. Having established this ratio, it is only necessary to add sufficient acid to keep the potassium, chromium and ferric iron in solution.

Similarly *sulphurous acid*, *hydrogen sulphide*, and *hydriodic acid* are oxidized at the ordinary temperature almost immediately; *oxalic acid* and *alcohol* on long standing, but quickly on heating; *hydrochloric* and *hydrobromic acids* only on warming.

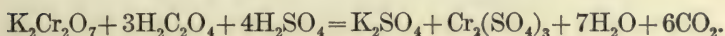
Sulphurous acid is oxidized to sulphuric acid:



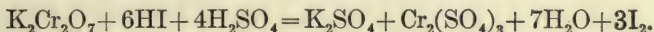
Hydrogen sulphide is oxidized to sulphur, which separates and makes the solution turbid:



Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is oxidized to carbonic acid:

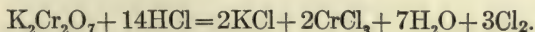


Hydriodic acid is oxidized to iodine:



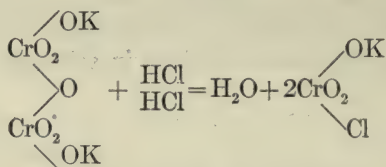
With all these reactions a change of color from yellow to green takes place, the *yellow chromate* being reduced to *green chromic salt*. In the case of the oxidation of hydriodic acid in the cold the solution will not become green, but brown, on account of the separation of iodine. If, however, the solution is heated to boiling, the iodine is volatilized and the green color appears.

Hydrochloric acid also is oxidized to chlorine by means of chromic acid:

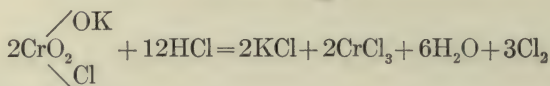


As this reaction takes place only on warming, it furnishes us with a convenient method for preparing small quantities of chlorine for analytical purposes, because the evolution of chlorine ceases as soon as the lamp is taken away. It is necessary, however, to em-

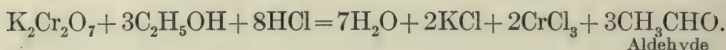
ploy an excess of hydrochloric acid, as otherwise no chlorine will be evolved owing to the formation of potassium chlorochromate:



which is decomposed on adding more hydrochloric acid:

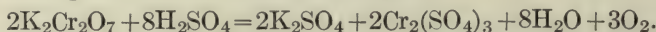


If alcohol and hydrochloric acid are allowed to act simultaneously upon a chromate (the reaction takes place on gentle warming without the evolution of chlorine), the alcohol is oxidized to aldehyde:

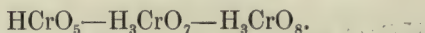


This last reaction is taken advantage of when it is desired to reduce a chromate, because the aldehyde (recognizable by its peculiar empyreumatic odor) and the excess of alcohol are easily removed by warming the solution, and the latter then contains simply the chromium and the metal of the chromate as chlorides.

By boiling chromates with concentrated sulphuric acid, reduction takes place with evolution of oxygen:



The behavior of *free chromic acid* towards *hydrogen peroxide* is characteristic. The chromic acid is converted into various blue-colored perchromic acids which are soluble in ether:



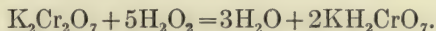
If a cold, alkaline solution of a chromate is treated with neutral hydrogen peroxide, the solution is colored red owing to the formation of an alkali salt of perchromic acid,  $\text{H}_3\text{CrO}_8$ :



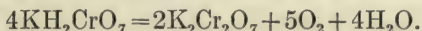
Little by little the red color disappears, with evolution of oxygen, and the yellow color of the chromate returns:



If a cold, aqueous solution of potassium dichromate is treated with hydrogen peroxide, the solution is colored violet due to the formation of the potassium salt of a slightly different perchromic acid,  $\text{H}_3\text{CrO}_7$ :

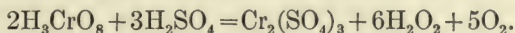


In this case, also, the violet color gradually disappears with evolution of oxygen and regeneration of the dichromate:



If either the red or violet solution, obtained as above described, is shaken with ether, the latter remains colorless.

The behavior of chromate solutions toward an excess of hydrogen peroxide in the presence of an excess of dilute sulphuric acid is quite different. There is then formed invariably the perchromic acid richest in oxygen,  $\text{H}_3\text{CrO}_8$ , and the solution is turned an intense blue. The blue color disappears after a short time and the solution turns green owing to the conversion of all the chromium into the chromic condition:



The perchromic acid is very soluble in ether and if the aqueous solution is shaken with ether the latter becomes colored a beautiful blue. The perchromic acid is more permanent in ethereal than in aqueous solution.

Since the formation of the intense-blue-colored perchromic acid takes place so readily, we have here a sensitive test for free chromic acid, which is made as follows: One or two cubic centimeters of hydrogen peroxide are treated with a few drops of dilute sulphuric acid and shaken with 2 c.c. of ether, after which a little of the chromate solution is added and the mixture again shaken. In the presence of 1/10 milligram of chromic acid, the upper liquid ether layer is colored intensely blue, and the reaction is noticeable with only 7/1000 milligram of chromic acid (Lehner).

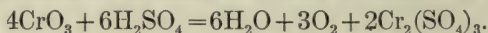
Most chromates are insoluble in water, and exhibit characteristic colors; therefore the easiest test for chromium is to change it to a chromate.

### Reactions for the Precipitation of Chromic Acid.

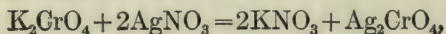
1. **Sulphuric Acid.**—*Dilute* sulphuric acid causes, at the most, a change of color from yellow to orange, without any evolution of gas.



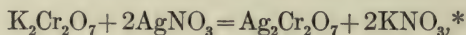
*Concentrated* sulphuric acid causes the cold solution to change to orange color, and there is often a separation of red needles of  $\text{CrO}_3$ ; the solution on being heated becomes green, the chromic acid being reduced to chromic salt with evolution of oxygen:



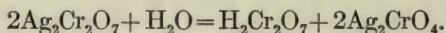
2. **Silver Nitrate** produces in neutral chromate solutions a brownish-red precipitate of silver chromate:



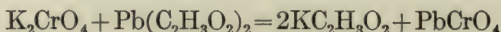
soluble in ammonia and mineral acids (hydrochloric acid changes it into insoluble silver chloride and chromic acid), insoluble in acetic acid. If to a moderately concentrated solution of potassium dichromate, silver nitrate be added, a reddish-brown precipitate of silver dichromate is formed:



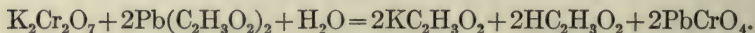
which, on being boiled with water, is changed into chromic acid and normal silver chromate:



3. **Lead Acetate** produces in solutions of normal chromates and dichromates a yellow precipitate of lead chromate, which is soluble in nitric acid but insoluble in acetic acid:

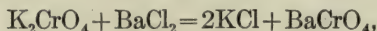


and



If lead nitrate is used instead of lead acetate, the precipitation is not complete unless sodium acetate is added.

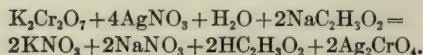
4. **Barium Chloride** produces in solutions of normal chromates a yellow precipitate of barium chromate:



soluble in mineral acids, insoluble in acetic acid. From solutions

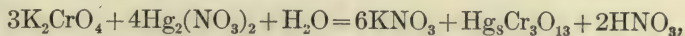
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\* In the presence of sodium acetate neutral silver chromate is precipitated:

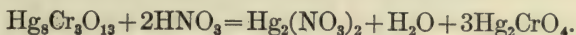


of dichromates the precipitation is complete only on addition of an alkali acetate (cf. page 74).

5. **Mercurous Nitrate** produces in the cold a brown precipitate of basic mercurous chromate:



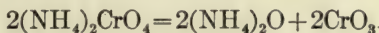
which on being boiled goes over into fiery-red, neutral mercurous chromate:



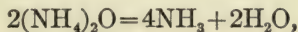
### Behavior of Chromium Trioxide and Chromates on Ignition.

As already mentioned, *chromium trioxide* is decomposed on ignition into chromic oxide and oxygen,  $2\text{CrO}_3 = \text{Cr}_2\text{O}_3 + \text{O}_3$ . The chromates of ammonium and mercury behave quite similarly. Thus *normal ammonium chromate* on ignition is changed to *chromic oxide, ammonia, nitrogen, and water*.

We can represent this reaction somewhat as follows: first, the chromate splits up into the basic and acid anhydrides:



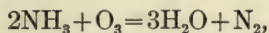
The ammonium oxide is broken up into ammonia and water, while the chromium trioxide is decomposed into chromic oxide and oxygen,



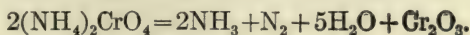
and



The oxygen, however, is used up immediately in oxidizing a part of the ammonia to water and nitrogen,



so that the whole reaction takes place according to the equation

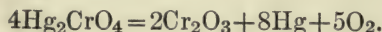


**Ammonium Dichromate** evolves only water and nitrogen:



This decomposition takes place violently with scintillation. The chromic oxide which remains behind is very voluminous and reminds one of tea-leaves; consequently it is sometimes called "tea-leaved oxide."

*Mercurous Chromate* is decomposed on ignition into *chromic oxide, metallic mercury, and oxygen*:

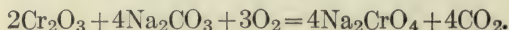


*The Dichromates of the Alkalies* are changed on ignition into normal chromate, chromic oxide, and oxygen:



#### REACTIONS OF CHROMIUM IN THE DRY WAY.

All chromium compounds color the borax, or salt of phosphorus, bead an emerald green both in the oxidizing and reducing flames. Heated with sodium carbonate on charcoal before the blowpipe, all chromium compounds yield a green slag, which after long heating is changed to green infusible chromic oxide. By fusing with soda and nitre in the loop of a platinum wire, all chromium compounds yield a yellow melt of alkali chromate:



If the fused mass is dissolved in water and acidified with acetic acid, the solution will give with silver nitrate a reddish-brown precipitate of silver chromate. This reaction is very delicate and serves for the detection of minute traces of chromium. Cloth which has been dyed with a chromium mordant can be tested in this way; the ash from a thread five cm. long is sufficient to give this test.

#### IRON, Fe. At. Wt. 55.84.

Sp. Gr. 7.88. M. Pt. about 1600° C.

*Occurrence*.—Native iron is rarely found. It occurs in basaltic rocks; also in meteorites, associated with nickel, cobalt, carbon, sulphur, and phosphorus.



The most important iron ores are the oxides and the sulphides. Of these may be mentioned:

Hematite,  $\text{Fe}_2\text{O}_3$ , isomorphous with corundum; magnetite  $\text{Fe}_3\text{O}_4$ , isomorphous with spinel; göthite,  $\text{FeHO}_2$ , isomorphous with diaspore and manganite; limonite,  $\text{Fe}_4\text{H}_6\text{O}_9$ ; (bog ore),  $\text{Fe}(\text{OH})_3$ , which is used in the purification of illuminating-gas; pyrite,  $\text{FeS}_2$ , which crystallizes in the isometric system; marcasite,  $\text{FeS}_2$ , orthorhombic. Iron disulphide is, therefore, dimorphous. Another important iron ore is siderite,  $\text{FeCO}_3$ , which is rhombohedral; Vivianite,  $(\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$ , is monoclinic.

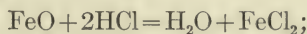
The metallic iron of commerce is never pure, but usually contains more or less *iron carbide*, *iron sulphide*, *iron phosphide*, *iron silicide*, corresponding *manganese* compounds and *graphite*, etc.

On dissolving commercial iron in acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ), hydrogen, contaminated with small amounts of hydrocarbons, hydrogen sulphide, mercaptans, phosphuretted hydrogen, and silicon hydride are given off, and the latter compounds give to the gas its unpleasant odor. There remains almost always an undissolved residue consisting chiefly of carbon.

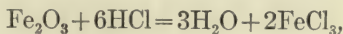
Iron is bivalent or trivalent, and forms the following oxides:

Iron protoxide Ferrous oxide	Iron sesquioxide Ferric oxide	Ferrous-ferric oxide.	Iron trioxide.*
$\text{FeO}$	$\text{Fe}_2\text{O}_3$	$\text{Fe}_3\text{O}_4$	$\text{FeO}_3$ .

Dissolving these oxides in acids, we obtain the corresponding iron salts; thus ferrous oxide gives with hydrochloric acid ferrous chloride,



ferric oxide gives ferric chloride,



while ferrous-ferric oxide yields a mixture of ferrous and ferric chlorides:



Iron, therefore, forms two series of salts: first, the ferrous, derived from ferrous oxide, containing bivalent iron; second, the ferric, derived from ferric oxide, containing trivalent iron. These

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\* Iron trioxide,  $\text{FeO}_3$ , containing hexavalent iron has never been isolated. It plays the part of an acid anhydride in ferrates of the general formula  $\text{R}_2\text{FeO}_4$ , which are decomposable by water.

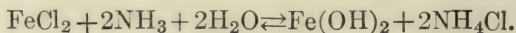
two series of salts show quite different behavior towards reagents. therefore, we will treat them separately.

### A. FERROUS COMPOUNDS.

Ferrous compounds, which may be prepared by dissolving metallic iron, ferrous oxide, ferrous hydroxide, ferrous carbonate, or ferrous sulphide, etc., in acids, are usually greenish in the crystallized state, but in the anhydrous condition they are white, yellow or bluish; in concentrated solution they are green; in dilute solutions almost colorless. Ferrous compounds exhibit a strong tendency to change over into ferric salts; they are strong reducing agents.

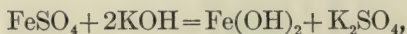
#### REACTIONS IN THE WET WAY.

1. **Ammonia** produces in neutral solutions an incomplete precipitation of white ferrous hydroxide:



Ferrous salts in this respect are similar to those of magnesium (cf. page 64). In the presence of ammonium chloride the reaction takes place in the direction from left to right; ammonia, therefore, causes no precipitation with ferrous salts out of contact with the air, provided sufficient ammonium chloride is present. On exposure to the air, however, a turbidity is soon formed, green at first, then almost black, and finally becoming brown. The small amount of ferrous hydroxide contained in the solution is oxidized by the air, forming at first black ferrous-ferric hydroxide and finally brown ferric hydroxide.

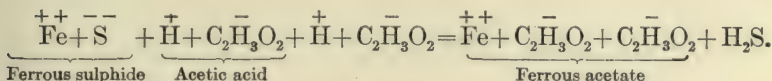
2. **Potassium and Sodium Hydroxides** produce, if air is excluded, complete precipitation of white ferrous hydroxide,



which is quickly oxidized by the air into ferric hydroxide.

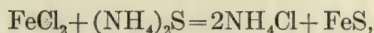
3. **Hydrogen Sulphide** produces no precipitation in acid solutions of ferrous salts; in dilute neutral solutions a small amount of black ferrous sulphide is precipitated; but if the solution contains *considerable alkali acetate*, hydrogen sulphide precipitates more of the iron as ferrous sulphide (but not all of it), in spite of the fact that ferrous sulphide is readily soluble in acetic acid. This interesting fact is an instructive illustration of the law of chemical mass action.

The solution of ferrous sulphide in acetic acid may be explained as follows: No substance is absolutely insoluble in water; but the amount dissolved cannot always be detected by chemical means, though it can be by physical methods. This small amount, in the case of a salt, is practically completely dissociated into its ions. If we allow acetic acid to act upon ferrous sulphide, the hydrogen ions from the acetic acid will unite with the negative sulphur ions from the ferrous sulphide, because hydrogen ions are never in equilibrium with sulphur ions except in the presence of undissociated hydrogen sulphide; the hydrogen sulphide is not very soluble in water and therefore escapes as a gas from the solution:



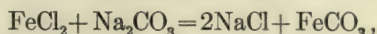
The equilibrium is disturbed by the escape of the gas; to restore it, more ferrous sulphide must go into solution, so that the above reaction is repeated until finally all of the ferrous sulphide has become dissolved. *The solution is effected by means of free hydrogen ions.* If, now, the concentration of the acetic ions is increased, the extent of the dissociation of the acetic acid will be lessened, in consequence of the law of chemical mass action. This means that there will be fewer hydrogen ions in the solution, so that the ferrous sulphide will be less soluble. The concentration of the acetate ions is increased by the addition of largely-dissociated alkali acetate.

**4. Ammonium Sulphide** precipitates iron completely as black ferrous sulphide:

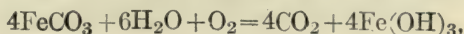


which is readily soluble in acids with evolution of hydrogen sulphide. In moist air it turns slightly brown, a part of the sulphur separates out, and a basic ferrous sulphide is formed.

**5. Alkali Carbonates** precipitate the white carbonate:



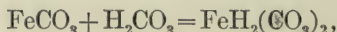
which in contact with the air becomes green, then brown:



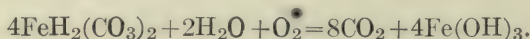


being converted into ferric hydroxide with loss of carbonic anhydride.

Ferrous carbonate is soluble in carbonic acid, forming ferrous bicarbonate:



a compound which is found in many natural waters, but which, like the normal carbonate, is decomposed by atmospheric oxygen with separation of ferric hydroxide:

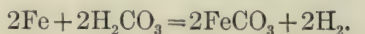


Consequently a mineral water which contains ferrous bicarbonate, if allowed to stand in contact with the air, will become turbid owing to the deposition of ferric hydroxide. To prevent this, the bottle must be filled with water and tightly corked so that no trace of air can get in. The ferric hydroxide is insoluble in carbonic acid.

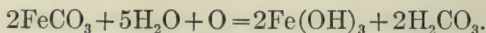
At this point we will say a few words with regard to the rusting of iron. Bright iron rusts if it comes in contact with moist air, as is well known. The process of rusting is a cyclical one, and three factors play an important part:

1. An acid;
2. Water;
3. Oxygen.

The process of rusting is usually started by an acid (even the weak carbonic acid suffices\*); the acid changes the metal into a ferrous salt with evolution of hydrogen:



Water and oxygen now act upon the ferrous salt, causing the iron in this salt to separate out as ferric hydroxide, *setting free the same amount of acid that was used in forming the ferrous salt*:

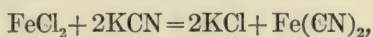



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\* Careful experiments by a number of able chemists have shown that even water itself dissolves iron slowly and the ferrous hydroxide thus formed is oxidized by dissolved oxygen with the formation of rust. Rusting takes place more rapidly, however, in the presence of a weak acid.

The acid which is set free again acts upon the metal, forming more ferrous salt, which is again decomposed, forming more rust. A very small amount of acid, therefore, suffices to rust a large amount of iron. The addition of alkali tends to stop rusting. It neutralizes any acid present, lessens the dissociation of water and thus its solvent action on iron, and also tends to make the metal passive.

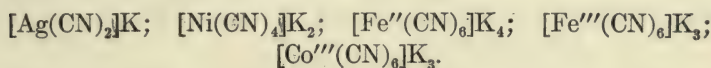
6. **Potassium Cyanide** precipitates yellowish-brown ferrous cyanide:



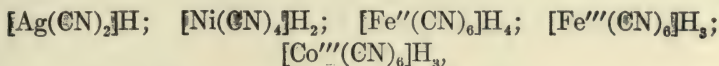
which is soluble in excess of the reagent, forming potassium ferrocyanide:



The potassium ferrocyanide (formed in the last reaction) is not a *ferrous* salt, but a *potassium* salt. It gives none of the above reactions for ferrous salts; so that the aqueous solution cannot contain ferrous ions, but K and  $\text{Fe}(\text{CN})_6$  ions. This property of the metallic cyanide forming with cyanides of the alkalis a complex salt, is a very common one. The cyanides of silver, nickel, iron (ferrous and ferric), and cobalt all dissolve in potassium cyanide, forming the following complex salts:



These compounds must be regarded as salts of the corresponding acids:

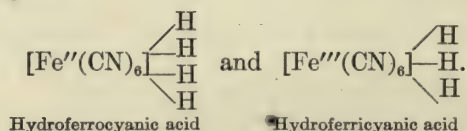


And it is possible, as a matter of fact, to isolate the last three acids, though the two former have never been prepared, as they immediately break down into metallic cyanide and hydrocyanic acid; just as carbonic acid is decomposed into water and carbon dioxide.

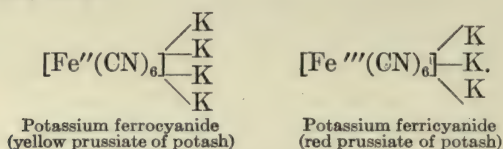
With iron, therefore, there are two series of complex cyanogen compounds, the ferrocyanides and the ferricyanides. The ferro-

cyanic derivatives contain the quadrivalent ferrocyanide group  $[\text{Fe}''(\text{CN})_6]_{\text{—}}$ , and the ferricyanides contain the trivalent ferricyanide group  $[\text{Fe}'''(\text{CN})_6]_{\text{—}}$ .

By saturating the free valencies with hydrogen, we obtain the corresponding acids:

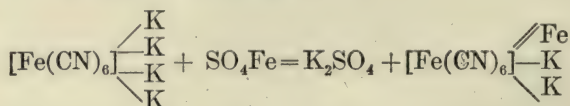


By substituting metals for the hydrogen atoms we obtain the corresponding salts:

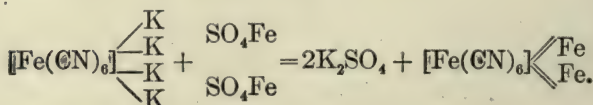


As has been mentioned, potassium ferrocyanide yields in aqueous solution the ferrocyanide ion  $[\text{Fe}''(\text{CN})_6]$  and potassium ions, while potassium ferricyanide yields ferricyanide  $[\text{Fe}'''(\text{CN})_6]$  and potassium ions. The solubility of their alkali and alkaline-earth salts, and the insolubility and color of the salts of the heavy metals (especially with both ferric and ferrous iron), are very characteristic of ferro- and ferricyanides.

7. **Potassium Ferrocyanide**,  $\text{K}_4\text{Fe}(\text{CN})_6$ , produces in solutions of ferrous salts, *with complete exclusion of air*, a *white* precipitate of *ferrous potassium ferrocyanide* or *ferrous ferrocyanide*, depending upon whether one or two molecules of ferrous salt react with one molecule of potassium ferrocyanide:

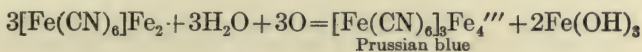


or

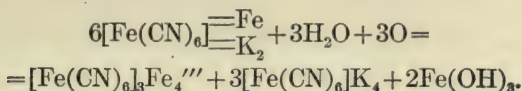




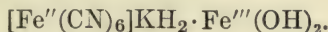
Although both of the above salts are white, a *light-blue* color is almost always obtained, because it is immediately oxidized somewhat by the air, forming the *ferric* salt of hydroferrocyanic acid (Prussian blue):



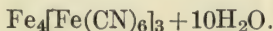
or



8. **Potassium Ferricyanide** added to solutions of ferrous salts yields blue compounds of different composition according to the relative amounts of the reacting substances and the temperature of the solution. When the *reagent* is in excess, *soluble* Turnbull's blue is formed from neutral solution which is identical with soluble Prussian blue\* and has the formula



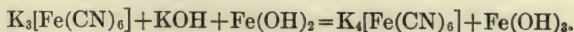
When an excess of *ferrous salt* is treated with potassium ferricyanide, *insoluble* Turnbull's blue is formed. The latter, in spite of contradiction in the literature, appears to be identical with insoluble Prussian blue and is the ferric salt of ferrocyanic acid and has the formula



The latter compound is always obtained at 15° C. when an excess of acid is not present. From hot, acid solutions complicated mixtures of different blue compounds are obtained. In forming the blue compounds the ferrous salt is usually oxidized by the potassium ferricyanide.

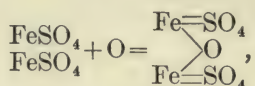
\* Hofmann, Heine, and Höchtlein, *Annalen*, 337 (1904), p. 1.

Potassium ferricyanide is a strong oxidizing agent in alkaline solution; it oxidizes ferrous hydroxide to ferric hydroxide and is itself reduced to ferrocyanide.

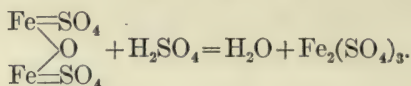


9. **Potassium Sulphocyanate** gives no reaction with ferrous salts (note difference from ferric salts).

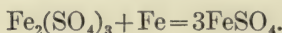
As has been stated, ferrous salts are oxidized by the air to ferric salts; thus ferrous sulphate is gradually changed into brown, basic ferric sulphate,



which is insoluble in water. Consequently it often happens that ferrous sulphate will not dissolve in water to a clear solution, but gives a brown turbid solution, becoming clear on the addition of acid; the basic ferric salt being changed to a soluble neutral salt:



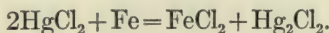
Such a solution, which then contains ferric sulphate, reacts with potassium sulphocyanate (cf. page 119). In order to free the solution from ferric salt, it may be boiled with metallic iron, with exclusion of air, whereby the ferric salt is changed into ferrous salt:



By means of strong oxidizing agents, ferrous salts can be quickly and completely changed into ferric salts, as was shown in the introduction (cf. pp. 4 and 5).

#### *Detection of Ferrous Oxide in the Presence of Metallic Iron.*

The mixture is treated with a large excess of a neutral solution of mercuric chloride and warmed on the water-bath, whereby the metallic iron goes into solution as ferrous chloride:



The residue is filtered off and the filtrate tested with potassium ferricyanide, a precipitate of Turnbull's blue showing that metallic iron was originally present.

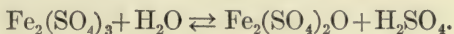
The residue is now washed with cold water, until all of the ferrous chloride has been dissolved out, and is then treated with

dilute hydrochloric acid.\* If the solution now gives a precipitate of Turnbull's blue with potassium ferrieyanide, ferrous oxide was present.

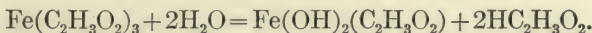
## B. FERRIC COMPOUNDS.

Ferric oxide,  $\text{Fe}_2\text{O}_3$ , is reddish brown, becomes grayish black on strong ignition, but on being pulverized appears red again.

The ferric salts are usually yellow or brown, but the ferric ammonium alum is pale violet. Ferric salts are yellowish brown in aqueous solution, and the solution reacts acid (hydrolysis). Dilution and warming favor the hydrolysis, so that all strongly-diluted ferric salts deposit basic salts on being boiled:



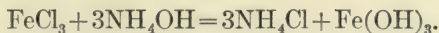
With ferric salts of the weaker acids, often all of the iron is precipitated as a basic salt; thus the acetate, on being boiled in a dilute solution, reacts as follows:



By the addition of acid all basic salts may be changed **back** into neutral salts.

### REACTIONS OF FERRIC SALTS IN THE WET WAY.

1. **Ammonia** precipitates brown, gelatinous ferric hydroxide:



Ferric hydroxide is readily soluble in acids. On ignition it loses water and is changed to oxide, which is very difficultly soluble in dilute acids. It is best brought into solution by long-continued heating with concentrated hydrochloric acid, at a moderately warm temperature.

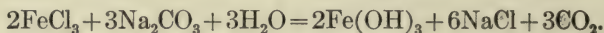
2. **Potassium** and **Sodium Hydroxide** also precipitate ferric hydroxide.

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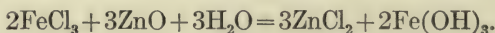
\* If hydrogen is given off, some metallic iron is still present; the experiment must be repeated and the mixture given a longer treatment with  $\text{HgCl}_2$  solution.



3. **Sodium Carbonate** produces a brown precipitate of basic carbonate, which at the boiling temperature is completely decomposed hydrolytically into hydroxide and carbon dioxide:

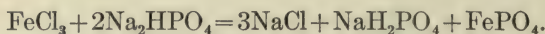


4. **Zinc Oxide** and **Mercuric Oxide** also precipitate the iron as hydroxide:

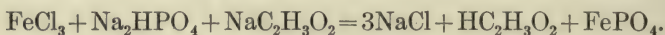


This reaction is frequently used in quantitative analysis.

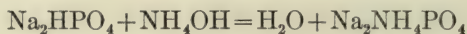
5. **Sodium Phosphate** precipitates yellowish-white ferric phosphate:



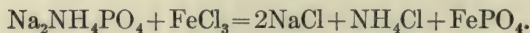
Ferric phosphate is insoluble in acetic acid, but readily soluble in mineral acids. The precipitation of iron with sodium hydrogen phosphate is consequently only complete when a large excess of the precipitant is employed, or when sodium acetate is added:



In this last case all the iron and all the phosphoric acid are precipitated. The reaction is often made use of in order to quantitatively precipitate phosphoric acid. An excess of the disodium phosphate will also cause complete precipitation of iron as phosphate, if the phosphate solution is previously exactly neutralized with ammonia:



and

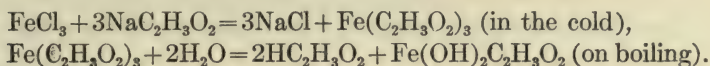


If, however, an excess of ammonia is added to the iron solution with the sodium phosphate, the precipitation of iron is incomplete, because the ferric phosphate dissolves in the excess of sodium phosphate, in the presence of ammonia (or ammonium carbonate), with a brown color and formation of a complex salt.

Ferric phosphate is transformed by ammonia into a brown basic

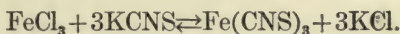
phosphate,\* and by potassium hydroxide almost completely into ferric hydroxide and potassium phosphate; while by *fusion* with caustic alkali or alkali carbonate it is completely decomposed.

6. **Alkali Acetates** produce in cold, neutral solutions a dark-brown coloration, and on boiling the dilute solution all of the iron separates as basic acetate:



The presence of organic hydroxy-acids (tartaric, malic, citric, etc.) and of polyatomic alcohols (glycerol, erythritol, mannitol, sugars, etc.) prevent all of the above-mentioned reactions, because complex salts are formed in which the iron is present in the form of a complex anion (cf. aluminium, page 92).

7. **Potassium Sulphocyanate, KCNS**, produces in solutions of ferric salts a blood-red coloration:



This action is reversible; the red color being most intense when an excess of ferric salt, or of potassium sulphocyanate is present.

If the solution is shaken with ether, the  $\text{Fe}(\text{CNS})_3$  goes into the ether. Ferric sulphocyanate combines readily with potassium sulphocyanate, forming complex potassium iron sulphocyanate:



analogous to potassium ferricyanide:



This complex salt is insoluble in ether, the  $\text{Fe}(\text{CNS})_3$  only being soluble therein; so that the red color is due to the formation of the ferric sulphocyanate and not to the complex salt.

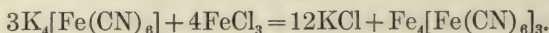
\* Then, if calcium ions are in solution, they are precipitated by the ammonium phosphate formed. In ammoniacal solutions, ferric ions do not prevent the precipitation of calcium as phosphate. This fact is often overlooked.

†  $\text{Fe}(\text{CNS})_6\text{K}_3 + 4\text{H}_2\text{O}$ . Cf. Rosenheim, *Z. anorg. Chem.* **27**, 208 (1901).

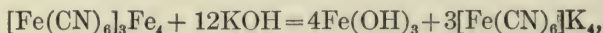
This reaction is extremely sensitive, but cannot always be relied on. If the solution contains considerable alkali acetate, the coloration cannot be recognized. The presence of organic hydroxy-compounds (tartaric acid, etc.) prevents the reaction in neutral solutions, but not in acid solutions. In the presence of mercuric chloride the red color disappears entirely; the mercuric chloride reacts with the ferric sulphocyanate, forming a colorless, soluble mercuric double salt:



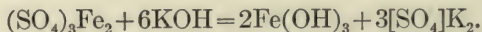
8. **Potassium Ferrocyanide**,  $\text{K}_4\text{Fe}(\text{CN})_6$ , produces in neutral or acid solutions of ferric salts an intense blue precipitation of Prussian blue:



Prussian blue, the ferric salt of hydroferrocyanic acid, is insoluble in water, but soluble in oxalic acid with a blue color (blue ink). It is also soluble in concentrated hydrochloric acid, but is precipitated again on dilution. As the ferric salt of hydroferrocyanic acid it behaves like other ferric salts to the hydroxides of the alkalies; ferric hydroxide and the alkali salt of hydroferrocyanic acid being formed:



similar to



Besides the *insoluble* Prussian blue, there exists a *soluble* Prussian blue, which is obtained by adding the ferric salt to an *excess* of potassium ferrocyanide.

The same compound is formed by adding a solution of ferrous salt to more than an equivalent amount of potassium ferricyanide. According to Hofmann, Heine, and Höchtern, this soluble blue has the formula \*



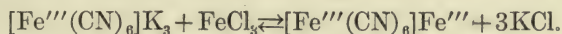

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\* Annalen, 337 (1904), p. 1.

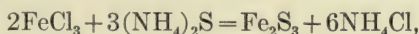


This substance, although soluble in water with a blue color, is insoluble in salt solutions. If, therefore, we desire to separate it from the solution, we "salt it out," *i.e.*, we add considerable salt to the solution (preferably potassium chloride), whereby it is changed to the insoluble form, and may be filtered from the solution.

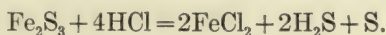
9. **Potassium Ferricyanide**,  $K_3[Fe(CN)_6]$ , produces no precipitation in solutions of ferric salts, only a brown coloration (differing from ferrous salts):



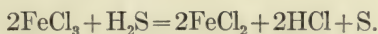
10. **Ammonium Sulphide**, added to a solution of a ferric salt, gives a precipitate of ferric sulphide,  $Fe_2S_3^*$ ,



which is soluble in cold, dilute hydrochloric acid, forming ferrous chloride and sulphur,

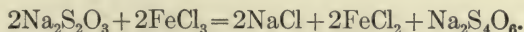


11. **Hydrogen Sulphide** reduces ferric salts to ferrous salts, with separation of sulphur:



Besides hydrogen sulphide, many other substances (nascent hydrogen, stannous chloride, sulphurous acid, hydriodic acid, etc.) will reduce ferric salts, as was shown on page 7.

12. **Sodium Thiosulphate**,  $Na_2S_2O_3$ , colors neutral ferric solutions a violet red, but the color disappears quickly and the solution then contains *ferrous* salt and *sodium tetrathionate*:




---

\* Louis Gedel, Ueber Schwefeleisen, Karlsruhe, 1905. Cf. also H. N. Stokes, J. Am. Chem. Soc. 29, 304 (1907). Hydrogen sulphide, passed into a barely acid solution of a ferric salt, precipitates some FeS; but if ammonia is added before introducing the hydrogen sulphide, no reduction takes place and all the iron is precipitated as  $Fe_2S_3$ .

The composition of the violet-red substance which is first formed is unknown; perhaps it is ferric *thiosulphate*.

As we have seen, there exist a number of iron compounds which contain the metal as a complex ion, so that it cannot be detected by the ordinary reagents. The complex hydroxy-organic compounds, as well as the ferro- and ferricyanide compounds, belong to this class of compounds,

If it is a question of proving the presence of iron in such a compound, a different method should be used in the case of an organic hydroxy-compound from that in the case of a ferro- or ferricyanide.

If organic substances are present, the iron is precipitated as sulphide by means of ammonium sulphide; or the organic matter is first removed by ignition, whereby metallic iron and carbon are obtained.

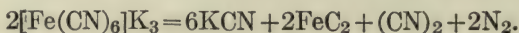
In case we have a ferro- or ferricyanide, the iron cannot even be precipitated by means of ammonium sulphide; the compound must be completely destroyed before it will be possible to detect the presence of iron by any of the ordinary methods.

This may be accomplished (a) by ignition, (b) by fusion with potash or soda, or (c) by heating strongly with concentrated sulphuric acid.

(a) *Decomposition by Ignition*.—The ferrocyanides are decomposed (with evolution of nitrogen) into potassium cyanide and carbide of iron:



The ferricyanides also leave behind iron carbide and potassium cyanide, but evolve cyanogen as well as nitrogen:

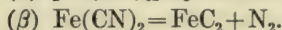
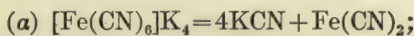


The residue from the ignition is treated first with water, whereby the potassium cyanide goes into solution, leaving behind the iron carbide; this is filtered off and treated with hydrochloric acid. The iron goes into solution as ferrous chloride, hydrocarbons are given off, and there remains some carbon.

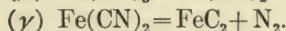
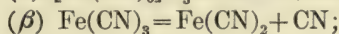
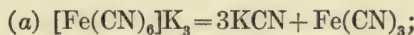
The above decomposition can be imagined to take place as follows:

By heating potassium ferrocyanide, it is decomposed first into

potassium cyanide and ferrous cyanide, while the latter on further heating is changed to iron carbide and nitrogen:



Potassium ferricyanide is decomposed into potassium cyanide and the very unstable ferric cyanide, which splits off cyanogen and becomes ferrous cyanide; the latter is decomposed, as before, into iron carbide and nitrogen:

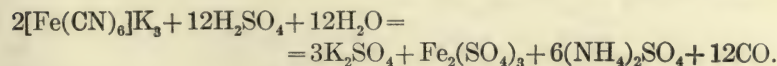
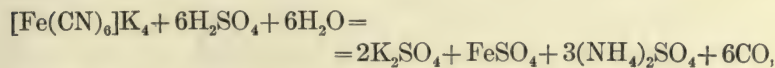


(b) *Decomposition by Means of Fusion with Potash.*—The substance is mixed with an equal amount of potash and heated in a porcelain crucible until the fusion is quiet. By this means a mixture of potassium cyanide and potassium cyanate (both soluble in water) is obtained in the presence of metallic iron:



The melt is therefore first treated with water, and the iron remaining behind is dissolved in hydrochloric acid.

(c) *Decomposition by Heating with Concentrated Sulphuric Acid.*—By heating with concentrated sulphuric acid all complex cyanogen compounds may be decomposed. By this means the metal present is changed into sulphate, the nitrogen of the cyanogen into ammonium sulphate, while the carbon of the cyanogen escapes as carbon monoxide:



The treatment with concentrated sulphuric acid is best accomplished in a porcelain crucible placed in an inclined position over the flame, and the flame directed against the upper part of the cru-



cible. The heating is continued until fumes of sulphuric acid cease to come off. The residue, which consists of an alkali sulphate, and ferrous or ferric sulphate (both being in an anhydrous condition), is treated with a little concentrated sulphuric acid, warmed somewhat, and water added little by little. In this way the sulphate is readily brought into solution; while with water alone solution takes place only with difficulty.

#### REACTIONS IN THE DRY WAY.

The borax (or sodium metaphosphate) bead, containing a small amount of an iron salt, is yellow while hot and colorless when cold in the oxidizing flame, and faint green in the reducing flame. When strongly saturated, however, the bead in the oxidizing flame is brown while hot, yellow when cold; and in the reducing flame it becomes bottle-green.

Heated on charcoal with soda before the blowpipe, all iron compounds leave a gray particle of metallic iron, which is usually difficult to see, but can be separated from the charcoal by means of the magnet. The reduction on the charcoal stick, as described on page 34, is a much more delicate test.

#### URANIUM, Ur. At. Wt. 238.5.

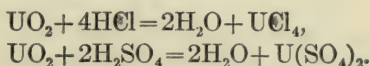
Sp. Gr. = 18.33. M. Pt. = 1500° C.

*Occurrence.*—Uranium occurs in nature chiefly in the mineral pitch-blende,  $U_3O_8$ ; but it is also found in a few rare minerals, uranite,  $(UO_2)_2CuP_2O_8 + 8H_2O$ ; samarskite (a niobite of iron, yttrium, cerium, and erbium with varying amounts of uranium); and liebigite,  $U(CO_3)_2 \cdot 2CaCO_3 + 10H_2O$ .

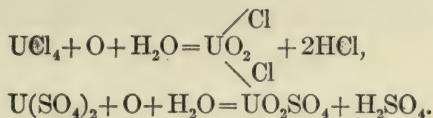
Klaproth showed, in 1789, that the mineral pitch-blende contained a new metal, which he called uranium. By heating the oxide with reducing agents he obtained a brown, almost copper-red, substance, which he took to be the metal, and it indeed does behave like a metal, dissolving in acids in contact with the air, forming yellowish-green salts.

It was not until 1842 that it was shown by Péligot that this reddish-brown body was not the metal uranium, but its dioxide. The hexavalent metal itself was obtained by Péligot, as a gray powder, by reducing the tetrachloride with sodium.

Out of contact with the air, uranium dioxide (uranyl) dissolves in strong acids, forming *uranous* salts.

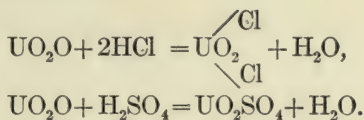


The uranous salts are extremely unstable, and on being exposed to the air change rapidly, forming *uranyl* salts:

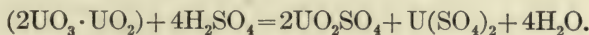


We will consider the reactions of the *uranyl* salts only. The uranous compounds are important for the quantitative determination of uranium itself, and will therefore be considered later.

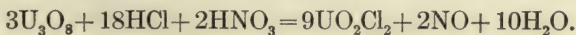
Besides uranyl (or uranium dioxide) uranium forms a trioxide,  $\text{UO}_3$ , which can be regarded as uranyl oxide,  $\text{UO}_2\text{O}$ . It dissolves in acids, forming uranyl salts:



By igniting the oxides of uranium in contact with air, dark-green urano-uranic oxide,  $\text{U}_3\text{O}_8$  or  $(2\text{UO}_3 \cdot \text{UO}_2)$ , is obtained, which out of contact with the air dissolves in strong acids, forming uranous and uranyl salts.



By dissolving in aqua regia, uranyl chloride is obtained:

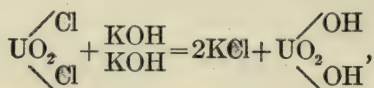


All uranyl compounds are colored yellow or yellowish green. Most of them are soluble in water, but the oxides, the sulphide, phosphate, and uranates are insoluble. In mineral acids all uranium compounds are soluble, with the exception of the ferrocyanide.

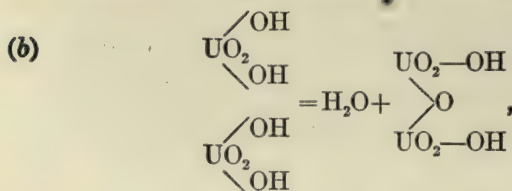
## REACTIONS OF URANYL COMPOUNDS IN THE WET WAY.

1. **Potassium Hydroxide** precipitates yellow amorphous **potassium uranate**. The reaction takes place in three stages:

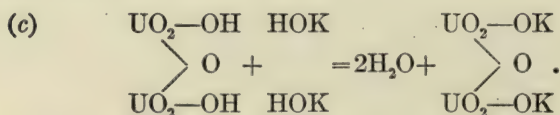
(a) At first uranyl hydroxide is formed,



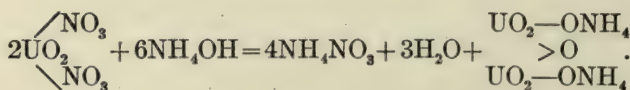
which immediately splits off water and becomes uranic acid,



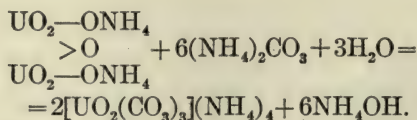
which combines with more potassium hydroxide and forms potassium uranate:



2. **Ammonia** precipitates yellow, amorphous **ammonium uranate**:



The alkali uranates are soluble in alkali carbonates, particularly in ammonium carbonate, with the formation of complex salts:

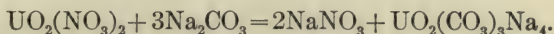


Consequently, in the presence of sufficient alkali carbonate, ammonia fails to precipitate uranium. Tartaric and citric acids (and



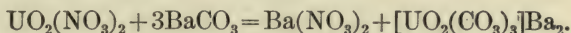
other organic substances) also prevent the precipitation with ammonia and caustic alkalis, as with iron, chromium, and aluminium.

3. **Sodium Carbonate** produces in concentrated solutions an orange-yellow precipitate of uranyl sodium carbonate:

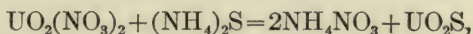


Uranyl sodium carbonate is soluble in *considerable* water, so that no precipitate is formed from dilute solutions. It is still more soluble in alkali carbonate solution, particularly in a bicarbonate solution. From such solutions sodium hydroxide precipitates the uranate, but ammonia does not.

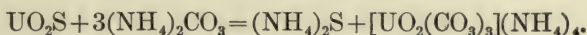
4. **Barium Carbonate** precipitates in the cold all of the uranium, probably as uranyl barium carbonate:



5. **Ammonium Sulphide** precipitates brown uranyl sulphide,

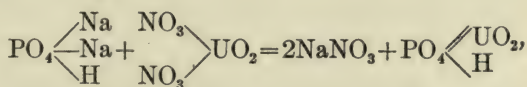


soluble in dilute acids and in ammonium carbonate:

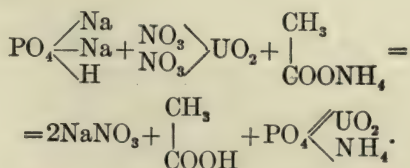


*Ammonium sulphide, therefore, produces no precipitate in solutions of uranyl salts in the presence of ammonium carbonate.*

6. **Sodium Phosphate** precipitates yellowish-white uranyl phosphate,

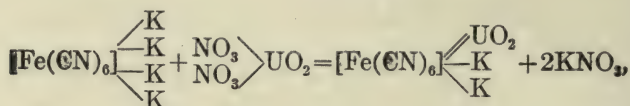


while, in the presence of ammonium acetate, uranyl ammonium phosphate is precipitated:

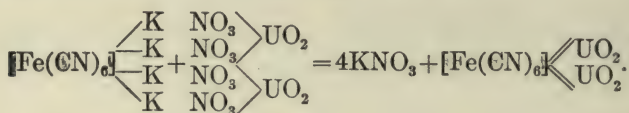


Both precipitates are insoluble in acetic acid, but soluble in mineral acids.

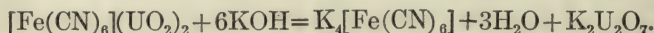
7. **Potassium Ferrocyanide** produces a brown precipitate, or, in very dilute solutions, a brownish-red coloration,



or by the action of two molecules of uranyl salt:



On addition of potassium hydroxide the brownish-red precipitate becomes yellow, owing to the formation of potassium uranate:



(Distinction from cupric ferrocyanide.)

#### REACTIONS IN THE DRY WAY.

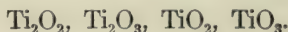
The borax (or sodium metaphosphate) bead is yellow in the oxidizing flame and green in the reducing flame.

#### TITANIUM, Ti. At. Wt. 48.1.

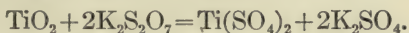
Sp. Gr. = 4.87.

*Occurrence.*—Titanium occurs in nature most frequently as the dioxide, rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic). Titanium is also found in the minerals perowskit,  $\text{TiO}_3\text{Ca}$ , titanite,  $\text{CaSiTiO}_5$ , and ilmenite,  $\text{FeTiO}_3$ , as well as in many crystalline rocks.

Titanium itself is a gray metal, very similar to iron. On being heated in the air it burns brightly to white titanium oxide. The following oxides of titanium are known:



The oxides  $Ti_2O_2$  and  $Ti_2O_3$  form violet-colored salts, which are readily changed by oxidizing agents into derivatives of  $TiO_2$ . The most important oxide is titanium dioxide, which sometimes acts as a base and sometimes as an acid. The titanium dioxide as it occurs in nature (rutile, etc.) is insoluble in all acids. In order to bring it into solution it is best to fuse it with potassium pyrosulphate, whereby it is changed into titanium sulphate:

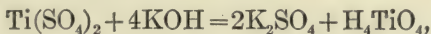


The melt is dissolved in *cold* water.

#### REACTIONS IN THE WET WAY.

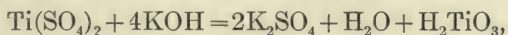
For these reactions a solution of titanium sulphate or of titanium hydroxide in hydrochloric acid may be used.

1. **Potassium Hydroxide** precipitates, in the cold, gelatinous *orthotitanic* acid,



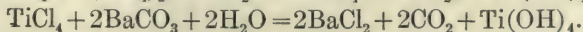
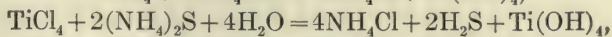
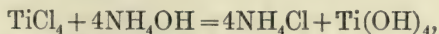
which is almost insoluble in an excess of the reagent, but readily soluble in mineral acids.

If the precipitation by potassium hydroxide takes place from a hot solution the titanium is precipitated as *metatitanic* acid,



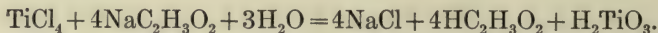
which is difficultly soluble in dilute acids. By long digestion with concentrated hydrochloric or sulphuric acid it goes gradually into solution. By the ignition of both these titanic acids the anhydride  $TiO_2$  is obtained, which is only slightly soluble in concentrated hydrochloric acid, but readily soluble in hot concentrated sulphuric acid.

2. **Ammonia, Ammonium Sulphide, and Barium Carbonate** (like potassium hydroxide) precipitate, in the cold, *orthotitanic* acid, readily soluble in acids; and from hot solutions the difficultly soluble *metatitanic* acid:



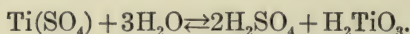


3. **Alkali Acetates** precipitate on boiling all of the titanium as metatitanic acid:



Titanium acetate is first formed, but it is completely decomposed hydrolytically by boiling the dilute solution.

4. **Water.**—Not only titanium acetate is hydrolytically decomposed by water, but all titanium salts. Use is made of this property in the separation of titanium from aluminium, iron, chromium, etc.; the oxides of these metals are fused with potassium pyrosulphate, the product of the fusion is dissolved in cold water,\* and the solution is then heated to boiling. The titanium is completely precipitated as granular metatitanic acid, which can be readily filtered off, while the remaining metals remain in solution as sulphates:



As this reaction, like all hydrolytic decompositions, is reversible, it is evident that, in order to make the precipitation of the metatitanic acid complete, *the amount of free acid present should be made as small as possible†, considerable water should be used, and the solution kept hot while filtering.*

In order to precipitate titanic acid from a solution according to this method, the concentrated solution is treated with sodium carbonate in the cold until a slight permanent precipitate of  $\text{Ti}(\text{OH})_4$  is obtained, sulphuric acid is added drop by drop until the precipitate is just dissolved, considerable water is added (300 to 500 c.c. of water should be used for each 0.1 gm.  $\text{TiO}_2$ ) and the solution kept at the boiling temperature for one hour. The granular metatitanic acid thus obtained is easy to filter as long as free acid is present. On being washed with pure water a turbid filtrate is always obtained; a little dilute sulphuric acid should therefore be added to the wash-water.

With the separation of titanium according to the above-described method, a play of colors will be observed in the bottom of the glass beaker or flask which is very characteristic of titanic acid.

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\* Solution takes place much more quickly if the liquid is kept in constant motion by conducting a current of air through it.

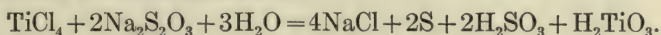
† If too little acid is present, however, iron and aluminium will precipitate.

The presence of tartaric acid, citric acid, and many other organic compounds prevents the above reactions. In such a case the organic substance must be first destroyed either by ignition or by oxidation with potassium permanganate (see pages 94 and 146), the titanium dioxide dissolved in sulphuric acid and precipitated according to any of the above methods.

5. **Potassium Ferrocyanide** produces in slightly acid solutions a brown precipitate.

6. **Tannin** produces a brown precipitate, which soon becomes orange.

7. **Sodium Thiosulphate** precipitates in boiling solutions all of the titanium as metatitanic acid:



8. **Sodium Phosphate** precipitates basic titanium phosphate  $\text{TiCl}_4 + 3\text{Na}_2\text{HPO}_4 + \text{H}_2\text{O} = 4\text{NaCl} + 2\text{NaH}_2\text{PO}_4 + \text{Ti}(\text{PO}_4)(\text{OH})$  soluble in mineral acids, insoluble in acetic acid.

9. **Hydrogen Peroxide**.—If hydrogen peroxide is added to a slightly acid solution of titanium sulphate, the solution is colored orange red, except in the presence of small amounts of titanium, when the color is light yellow. This reaction, which depends upon the formation of  $\text{TiO}_3$ , is exceedingly delicate, and is especially suitable for the detection of titanium in rocks. Vanadic acid behaves similarly with hydrogen peroxide.

If a solution of titanium sulphate is treated with a large excess of hydrogen peroxide and then potassium hydroxide is added, a precipitate is formed which dissolves in a great excess of the alkali, forming a yellow solution. This solution remains clear for a long time but eventually a bright yellow precipitate of  $\text{Ti}(\text{OH})_6$  is formed.\*

An insoluble titanium compound on being fused with sodium peroxide in a nickel crucible yields a melt which permits the extraction of all the titanium by water.† If the solution is made strongly acid with sulphuric acid, the orange-red color of pertitanic acid is apparent. If iron was present in the original insoluble titanium mineral, it is left insoluble in water after the fusion with sodium peroxide.

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\* A. Classen, Ber. 21, 371 (1888).

† J. H. Walton, Jr., J. Am. Chem. Soc. 1907.

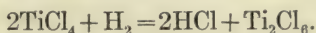
TABLE I. SEPARATION OF IRON, ALUMINIUM, CHROMIUM, AND URANIUM.

The metals are assumed to be in solution in the form of chlorides. Sodium or potassium hydroxide is added to the solution (in a porcelain dish) until it reacts strongly alkaline; it is heated to boiling, diluted with hot water, the boiling continued two to three minutes, and filtered.

PRECIPITATE.	SOLUTION.
<p>The precipitate contains <math>\text{Fe}(\text{OH})_3</math>, <math>\text{Cr}(\text{OH})_3</math>, <math>\text{Na}_2\text{U}_2\text{O}_7</math>. It is washed four times with hot water, dissolved in as little hydrochloric acid as possible, treated with an excess of ammonium carbonate, heated just to the boiling-point, and filtered.</p>	<p>The solution contains <math>\text{Al}(\text{ONa})_3</math>. Hydrochloric acid is added drop by drop. The solution becomes turbid when sufficient hydrochloric acid has been added, aluminium hydroxide being precipitated:  <math>\text{Al}(\text{ONa})_3 + 3\text{HCl} = 3\text{NaCl} + \text{Al}(\text{OH})_3</math>.</p> <p>The addition of hydrochloric acid is continued until the solution is clear. Ammonia is added to the clear acid solution, which is now boiled and the precipitated <i>aluminium hydroxide</i> (white gelatinous precipitate) is filtered off. A small portion of the precipitate is heated with cobalt nitrate, as described on page 95. <i>Thénard's blue</i> shows the presence of <i>aluminium</i>.</p>
<p>The precipitate now contains <math>\text{Fe}(\text{OH})_3</math> and <math>\text{Cr}(\text{OH})_3</math>.  <i>Test for iron:</i> A small portion of the precipitate is dissolved in a few drops of hydrochloric acid diluted with water, and a few drops of potassium ferrocyanide added; a <i>dark-blue precipitate of Prussian blue</i> shows the presence of <i>iron</i>.</p> <p><i>Test for chromium:</i> Another portion of the precipitate is mixed with some sodium carbonate and potassium nitrate, placed in a platinum spiral and fused in the upper oxidation zone of the non-luminous gas-flame. After cooling, the fused mass is crushed on porcelain with a pestle, dissolved in water, acidified with acetic acid, and a few drops of silver nitrate added. A <i>red precipitate of silver chromate</i> shows the presence of <i>chromium</i>.</p>	<p>The solution contains <math>[(\text{UO}_2)(\text{CO}_3)_3](\text{NH}_4)_4</math>. It is acidified with hydrochloric acid and a few drops of potassium ferrocyanide added; a <i>brown precipitate or coloration</i> shows the presence of <i>uranium</i>.</p>

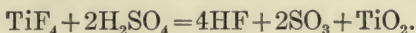


10. **Zinc** or **Tin** produces in acid solutions, preferably with hydrochloric acid, a violet color caused by the formation of  $Ti_2Cl_6$ :



The quadrivalent titanium compounds are *not* reduced by hydrogen sulphide or sulphurous acid.

11. **The Fluoride** is quantitatively changed to the dioxide by evaporation with sulphuric acid (Difference from silicic acid).



#### REACTIONS IN THE DRY WAY.

Titanium compounds do not color the borax, or sodium metaphosphate, bead in the oxidizing flame; after continued heating in the reducing flame the bead becomes yellow while hot and violet when cold. By the addition of a little tin the violet color appears much more quickly. The addition of iron causes a brownish to red bead.

On fusing titanic acid with sodium carbonate, sodium metatitanate is formed, which is readily soluble in acids. By treatment with *hot* water, sodium metatitanate is decomposed, forming metatitanic acid, which is difficultly soluble in dilute acids. Even in cold water hydrolysis of sodium titanate takes place and none of the titanium dissolves.

**MANGANESE, Mn.** At. Wt. 54.93.

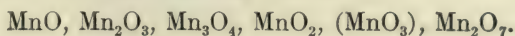
Sp. Gr. = about 8.0. M. Pt. = 1245° C.

*Occurrence.*—The most important manganese minerals are pyrolusite,  $MnO_2$ , orthorhombic; polianite, also  $MnO_2$ , tetragonal, isomorphous with rutile and tinstone; braunite,  $Mn_2O_3$ , tetragonal; manganite,  $Mn\begin{smallmatrix} \diagup O \\ \diagdown OH \end{smallmatrix}$ , orthorhombic, isomorphous with göthite and diaspore; hausmannite,  $Mn_3O_4$ , tetragonal; and rhodochrosite,  $MnCO_3$ .

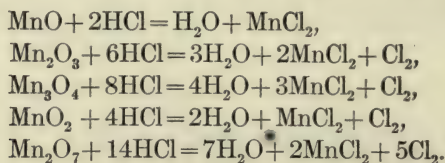
Manganese is a constant companion of iron, so that we find it in varying amounts in almost all iron ores.

It is a grayish-white metal which is readily oxidized in moist air, and is attacked by dilute acids, even acetic acid.

Manganese forms the following oxides:

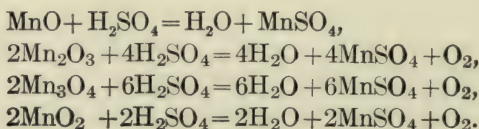


By treating these oxides in the cold with dilute hydrochloric acid a dark greenish-brown solution is obtained, except in the case of MnO, which dissolves clear; but on warming, a clear solution is obtained in all cases, with evolution of chlorine, particularly after dilution. The solution then contains a bivalent manganese salt:



In the cold the unstable higher chlorides are formed, which on warming lose chlorine and become manganous chloride.\*

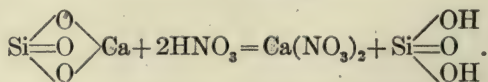
All manganese oxides dissolve on warming with concentrated sulphuric acid, forming manganous sulphate, accompanied (with the exception of MnO) by evolution of oxygen:



The behavior of the higher oxides, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, and Mn<sub>3</sub>O<sub>4</sub>, with boiling dilute nitric or sulphuric acid is very interesting: MnO<sub>2</sub> is not attacked at all by these dilute acids; while Mn<sub>2</sub>O<sub>3</sub> gives up half of its manganese to the acid, the other half remaining undis-

solved as brown hydrated manganese dioxide,  $\text{Mn} \begin{smallmatrix} \diagup \text{OH} \\ = \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$ ; two thirds of Mn<sub>3</sub>O<sub>4</sub> is dissolved by these acids, brown hydrated manganese dioxide being left behind, as before.

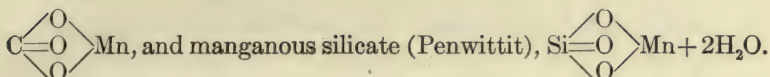
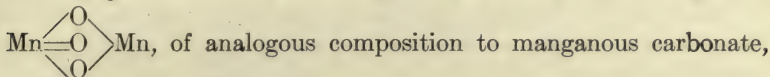
This  $\text{Mn} \begin{smallmatrix} \diagup \text{OH} \\ = \text{O} \\ \diagdown \text{OH} \end{smallmatrix}$  separates out just as silicic acid is deposited from a silicate on the addition of a strong acid:



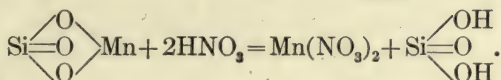
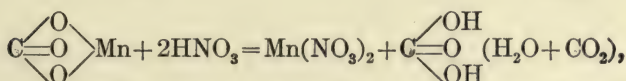
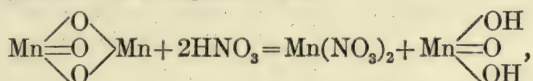
\* Neumann isolated [MnCl<sub>5</sub>](NH<sub>4</sub>)<sub>2</sub>. Monatshefte, 1894, p. 492.

In fact, hydrated manganese dioxide behaves in most cases exactly like an acid, the oxides  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  behave like manganous salts of this acid and are to be regarded as manganites.\*

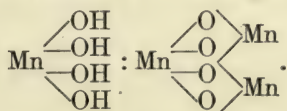
$\text{Mn}_2\text{O}_3$  is, therefore, to be regarded as manganous manganite,



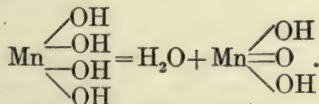
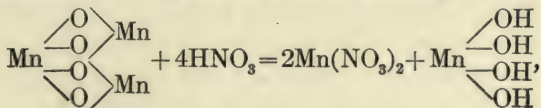
According to this conception it is easy to understand why  $\text{Mn}_2\text{O}_3$  gives up half of its manganese on treatment with dilute nitric acid, with the separation of manganous acid:



$\text{Mn}_3\text{O}_4$ , which gives up two thirds of its manganese, must be considered to be the derivative of orthomanganous acid:



On treatment with nitric acid the ortho acid first separates out; it loses water, and goes over into metamanganous acid:



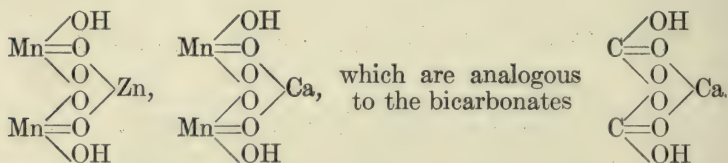
\*  $\text{Mn}_2\text{O}_3$ , however, also plays the part of a basic anhydride, forming a sulphate,  $\text{Mn}_2(\text{SO}_4)_3$ , which is decomposed by water into sulphuric acid and  $\text{Mn}_2\text{O}_3$ . Furthermore, potassium-manganese and ammonium-manganese alums are known.



$\text{MnO}_2$  stands in the same relation to  $\text{H}_2\text{MnO}_3$  as  $\text{CO}_2$  to  $\text{H}_2\text{CO}_3$ , as  $\text{SiO}_2$  to  $\text{H}_2\text{SiO}_3$ , and as  $\text{SnO}_2$  to  $\text{H}_2\text{SnO}_3$ ;  $\text{MnO}_2$ , therefore, behaves like an acid anhydride and is isomorphous with tinstone,  $\text{SnO}_2$ , crystallizing as polianite in the tetragonal system.

Like  $\text{SnO}_2$  (which see), manganese dioxide behaves partly as an acid anhydride and partly as the anhydride of a base, because it probably forms the chloride  $\text{MnCl}_4$ . For if  $\text{MnO}_2$  is treated with cold concentrated hydrochloric acid it dissolves with a brownish-green color, forming manganese tetrachloride, soluble in ether with a green color. If, therefore, the solution is shaken with ether, the upper layer is colored green.

Not only manganous manganites are known, but quite a number of other manganites. Some of these play a very important part in analytical chemistry; as, for example, zinc and calcium bimanganites:



Zinc bimanganite is formed in the volumetric determination of manganese (see Vol. 2). Calcium bimanganite is of importance technically. Thus the recovery of manganese, by the Weldon process, in the manufacture of chlorine, depends upon the formation of calcium bimanganite.

Manganous oxide,  $\text{MnO}$ , is the only oxide of manganese which in all cases acts as the anhydride of a base. By dissolving this oxide in acids, manganous salts are always obtained, in which the manganese is bivalent. The oxide  $\text{MnO}_3$  has never been isolated, but there are salts ( $\text{R}_2\text{MnO}_4$ , see page 143) known which are derived from it.  $\text{Mn}_2\text{O}_7$  is a distinct acid anhydride, from which the permanganates ( $\text{RMnO}_4$ ) are derived.

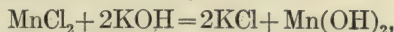
In the study of the reactions of manganese we will consider first the manganous compounds, then the manganates and permanganates.

### A. Manganous Compounds.

The manganous compounds are colored pink both in the crystalline state and in aqueous solution; but in the anhydrous state they are colorless with the exception of the sulphide.

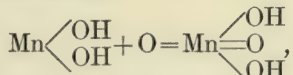
#### REACTIONS IN THE WET WAY.

1. **Potassium or Sodium Hydroxide** precipitates **white manganous hydroxide**,

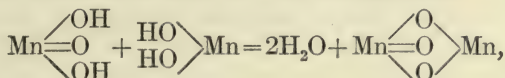


which rapidly becomes brown in the air, owing to the formation of manganous manganites:

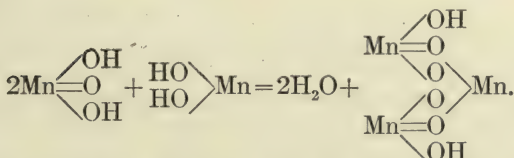
First of all, a part of the manganous hydroxide is oxidized by the air to manganous acid:



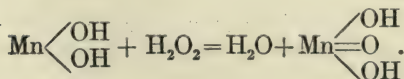
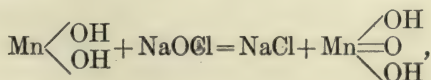
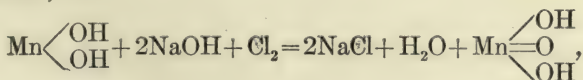
which, on coming in contact with the basic manganous hydroxide, immediately forms salts with it—the manganites,



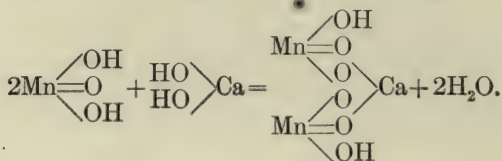
or



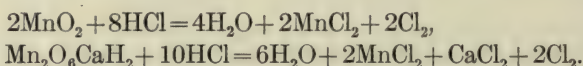
This oxidation takes place in the air only gradually, but immediately in the presence of chlorine, bromine, hypochlorites, hydrogen peroxide, etc.:



The formation of manganites is of technical importance, as mentioned on page 136. The residue obtained in the preparation of chlorine from pyrolusite and hydrochloric acid consists chiefly of manganese chloride, and is precipitated by the addition of lime, manganous hydroxide being formed. This mixture of manganous hydroxide and lime is exposed to the action of the atmosphere, whereby manganous acid is formed, which unites with the calcium as the stronger base, forming calcium bimanganite, so that finally all of the manganese is oxidized to manganous acid:

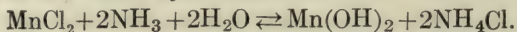


On treating the residue, when in the right condition, with hydrochloric acid again, the same amount of chlorine is obtained as from the original pyrolusite:



It is, however, necessary to add a little more hydrochloric acid in the latter case, because a part of the acid is used up in setting the manganous acid free from the manganite.

**2. Ammonia** precipitates (as with magnesium and ferrous salts) from neutral solutions free from ammonium salts a part of the manganese as the white hydroxide

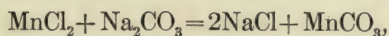


If sufficient ammonium chloride is present, ammonia causes no precipitation. The greater part of the manganese then remains in solution as manganous chloride, but a small amount exists as the hydroxide. On standing in the air, this dissolved hydroxide is changed into the more difficultly soluble manganous acid which is deposited in brown flocks. The condition of equilibrium in the solution is thereby disturbed, and in order to restore it more hydroxide is formed, and the reaction continues in this way until finally all of the manganese is precipitated. This fact must be considered in the separation of manganese from ferric iron, aluminium, etc. If a solution of ferric and manganous chlorides contains sufficient

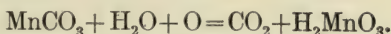


ammonium chloride, none of the manganese and all of the iron will be precipitated on the addition of ammonia, but if the solution stands in contact with the air little by little the manganese will be precipitated. In effecting the separation, therefore, an excess of ammonium chloride should be present, the solution boiled to remove the air as much as possible from the solution, then a *slight* excess of ammonia should be added and the solution filtered *immediately*. The separation even then is not quantitative, but is satisfactory for qualitative analysis.

3. **Alkali Carbonates** precipitate white manganous carbonate,



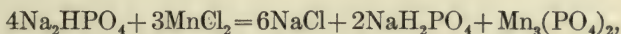
which after long boiling is changed by the oxygen of the air into hydrated manganese dioxide:



4. **Ammonium Carbonate** precipitates even in the presence of ammonium salts the white carbonate (difference from magnesium).

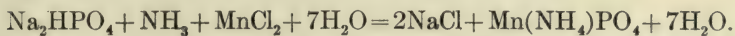
5. **Barium Carbonate** produces a precipitate only in hot solutions.

6. **Sodium Phosphate** precipitates white tertiary manganous phosphate,



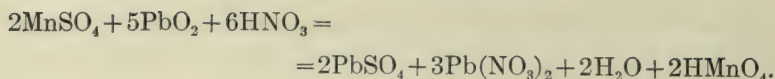
soluble in mineral acids and in acetic acid.

If to the boiling solution of this precipitate in acid an excess of ammonia is added, manganous ammonium phosphate will be precipitated, as with magnesium (see page 65):

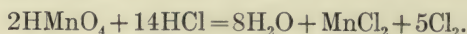


The precipitate consists of pink scales, and is insoluble in water.

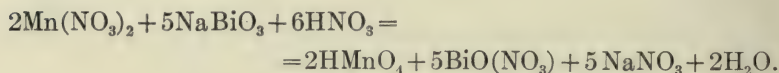
7. **Lead Peroxide and Concentrated Nitric Acid.** (Volhard's reaction).—If a solution containing only traces of manganese is boiled with lead peroxide and concentrated nitric acid, then diluted with water and the residue allowed to settle, the supernatant liquid acquires a distinct violet-red color, owing to the formation of permanganic acid:



This extremely delicate reaction does not take place in the presence of much hydrochloric acid or chlorides, because the permanganic acid is thereby destroyed:

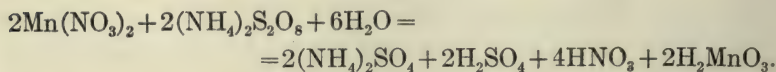


8. **Sodium Bismuthate** added to a cold solution of a manganous salt in dilute nitric acid (about sp.gr. 1.13) causes the formation of permanganic acid. The reagent, which corresponds approximately to the symbol  $\text{NaBiO}_3$ , is prepared by fusing bismuth oxide with sodium peroxide; it is insoluble in water and the excess of reagent may be filtered off through asbestos after applying the test. The reaction may be expressed by the equation:



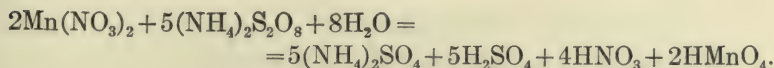
The test is extremely delicate when nothing is present that will react with the permanganate formed. An insoluble carbonaceous residue, such as remains after the solution of cast iron in acid, must be filtered off before adding the reagent. If the solution is heated, the permanganic acid breaks down and hydrated manganese dioxide is precipitated.

9. **Ammonium Persulphate.** If a solution of a manganous salt in either dilute sulphuric or nitric acid is treated with ammonium persulphate, all the manganese is gradually oxidized to the quadrivalent condition and a precipitate of hydrated manganese dioxide (manganous acid) is formed:



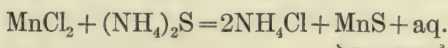
If, however, the solution contains a trace of silver nitrate,

then the oxidation goes farther and permanganic acid is formed:



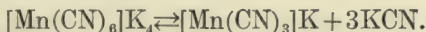
This reaction is quantitative for small amounts of manganese and in the absence of anything that will react with the permanganic acid.\*

10. **Ammonium Sulphide** precipitates from manganese solutions flesh-colored hydrated manganese sulphide:



On boiling with a large excess of ammonium sulphide it is changed into less hydrated *green* manganese sulphide of the formula,  $3\text{MnS} + \text{H}_2\text{O}$ .

11. **Potassium Cyanide**.—On adding potassium cyanide to a solution of a manganous salt a brownish precipitate appears, which redissolves in an excess of potassium cyanide, forming a brownish-colored solution. From this solution there separates, on standing or warming, a voluminous green precipitate of  $[\text{Mn}(\text{CN})_3]\text{K}$ , which dissolves in still more potassium cyanide, forming a yellow solution of  $[\text{Mn}(\text{CN})_6]\text{K}_4$ . This salt is very unstable; it can exist only in the presence of considerable potassium cyanide. Consequently, on diluting the yellow solution with water, the green salt again separates out:



On heating the dilute solution to boiling, the manganous potassium cyanide is completely decomposed into potassium cyanide, hydrogen cyanide, and insoluble white manganous hydroxide, which precipitates.



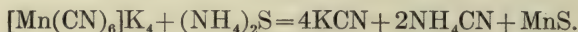
The manganous potassium cyanide is not precipitated by ammonium sulphide in the presence of considerable potassium cyanide:

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\* Cf. M. Marshall, Z. anal. Chem. **43**, 418, 655 (1904).



but the diluted solution, on the contrary, readily deposits the manganese as sulphide on boiling:

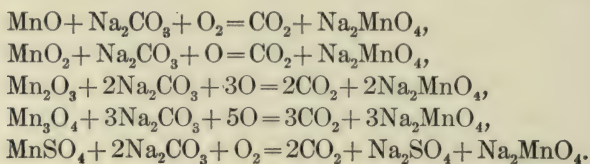


This reaction offers a convenient means for separating manganese from nickel, because nickel potassium cyanide is not precipitated by ammonium sulphide on boiling the dilute solution.

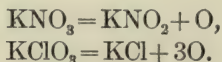
#### REACTIONS IN THE DRY WAY.

The bead of borax, or salt of phosphorus, is amethyst red in the oxidizing flame with small amounts of manganese, almost brown with larger amounts, and can then be mistaken for the nickel bead. Heated in the reducing flame, the manganese bead becomes colorless, while the nickel bead appears gray.

On fusing any manganous compound with caustic alkali or alkali carbonate (on platinum foil) in the air, or, better still, in the presence of an oxidizing agent (such as potassium nitrate, potassium chlorate, etc.), a green melt is obtained, owing to the formation of the alkali salt of manganic acid, as is shown by the following equations:

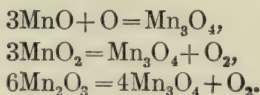


The oxygen comes either from the air or from the nitrate or chlorate:



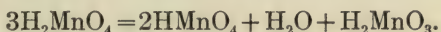
This reaction is exceedingly delicate, for a fraction of a milligram can be recognized by the formation of this green color.

By ignition in the air the oxides of manganese are changed to  $\text{Mn}_2\text{O}_4$ :

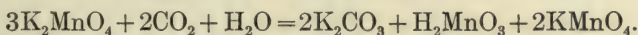


### B. Manganic and Permanganic Acids.

The free manganic acid has never been isolated. If we attempt to form it from the green melt of the alkali manganate by the addition of acid, permanganic acid and hydrated manganese dioxide will be obtained; a part of the unstable manganic acid oxidizes another part of the same to permanganic acid, while the oxidizing part is itself reduced to hydrated manganese dioxide:



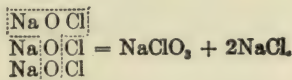
This transformation takes place so readily that the green solution of the manganate is changed to a reddish-violet solution of a permanganate by simply standing in the air with the help of the carbonic acid which the air always contains:



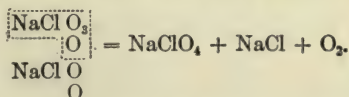
The reaction takes place much more rapidly, however, if a few drops of a strong acid are added.\*

\* The above-mentioned reaction, in which an oxygen compound is decomposed into a compound richer in oxygen, and at the same time into one poorer in oxygen, or, in other words, a part of the compound is oxidized at the expense of the oxygen of another part, is so common that we will give a few other typical examples at this place.

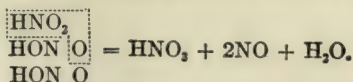
The hypochlorites are changed, by warming the aqueous solution, into chlorate and chloride:



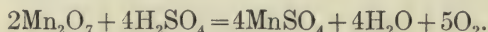
By igniting the chlorate a perchlorate and a chloride are formed:



Nitrous acid is changed in aqueous solution into nitric acid and nitric oxide-



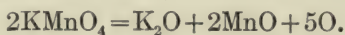
**Permanganic Acid**,  $\text{HMnO}_4$ , although much more stable than manganic acid, is only known in aqueous solution; but the anhydride  $\text{Mn}_2\text{O}_7$ , on the other hand, has been isolated. On cautiously adding concentrated sulphuric acid to the cooled solution of a permanganate, oily drops of reddish-brown  $\text{Mn}_2\text{O}_7$  separate out, which, however, on being warmed (the heat of reaction is sufficient) explode with scintillation:



The salts of permanganic acid (the permanganates) are all soluble in water, with a reddish-violet color, and are very energetic oxidizing agents.

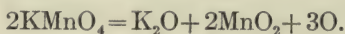
According to whether the oxidation takes place in acid or in alkaline solution the permanganic acid is reduced either to manganous salt or to  $\text{MnO}_2$ .

The oxidation in acid solution takes place according to the following scheme:



It is only necessary to provide sufficient acid to dissolve the oxides formed.

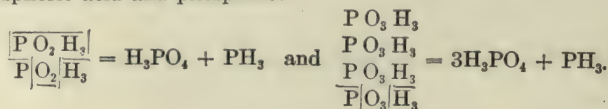
The oxidation in alkaline solution reduces the permanganic acid only to manganese dioxide:



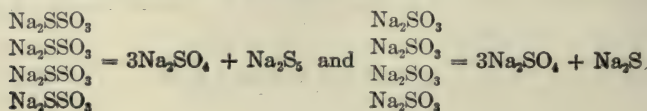

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*Examples of Oxidation in Acid Solution.*—The oxidation of

Hypophosphorous acid and phosphorous acid are changed on warming into phosphoric acid and phosphine:



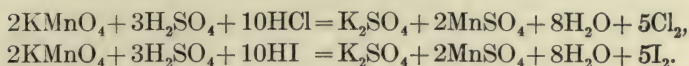
Similarly the alkali thiosulphates and alkali sulphites are changed on ignition in the absence of air into sulphate and sulphide:



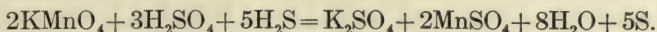


ferrous salts by potassium permanganate has been explained (see page 5); but we will mention here a few other important cases.

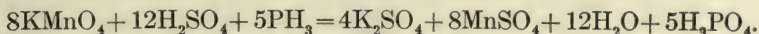
Almost all hydrogen compounds of the negative elements are oxidized by a solution of potassium permanganate, hydrochloric and hydrobromic acids on warming, hydriodic acid even in the cold.\*



Hydrogen sulphide is oxidized in the cold with separation of sulphur:

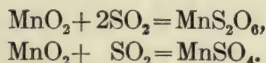


The hydrogen compounds of phosphorus, arsenic, and antimony are oxidized to the corresponding acids:



Sulphurous acid decolorizes the solution of potassium permanganate, sulphur and dithionic acid being always formed. It is never possible by means of this reaction to oxidize sulphurous acid completely to sulphuric acid. The proportion of sulphuric acid formed to that of dithionic acid varies with the concentration and with the temperature; consequently sulphurous acid cannot be determined quantitatively by means of potassium permanganate.

If sulphurous acid is allowed to act upon manganese dioxide suspended in water, manganese dithionate and manganese sulphate are formed:



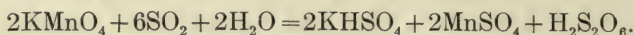
In the cold more of the dithionate is formed, while on warming more sulphate.

As a point must be reached in the oxidation of sulphurous acid

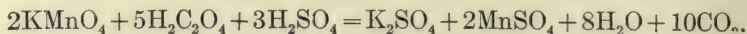
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\* The manganese in the permanganate ion has a valence of seven, which represents seven positive electric charges. The chlorine, bromine, or iodine has one negative charge, but when this charge is neutralized (*i.e.*, oxidized) electrically neutral halogen results.

by potassium permanganate where  $\text{MnO}_2$  begins to act upon the former, there must, therefore, always be some dithionic acid formed. At a certain temperature and with a definite concentration, the reaction can take place as follows:

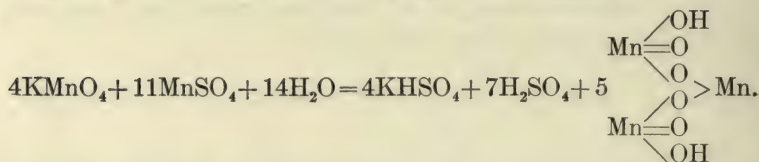


*Oxalic Acid* is completely oxidized on warming to carbonic anhydride:



Tartaric acid is also oxidized by permanganates.

In the case of all the above reactions, a considerable excess of acid must be present, otherwise the solution will become turbid, owing to the formation of brown manganous manganite:



According to the concentration and temperature at which the reaction takes place other manganites may be formed.

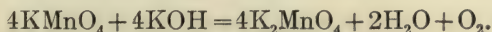
*Hydrogen Peroxide*, or the peroxides of the alkalies and alkaline earths, as well as percarbonic acid, all decolorize permanganic acid; the permanganic acid is reduced and half the oxygen evolved comes from it.

1.  $2\text{KMnO}_4 + 5\text{H}_2\text{O}_2 + 4\text{H}_2\text{SO}_4 = 2\text{KHSO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2.$
2.  $2\text{KMnO}_4 + 5\text{K}_2\text{C}_2\text{O}_6 + 14\text{H}_2\text{SO}_4 =$   
 $= 12\text{KHSO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 10\text{CO}_2 + 5\text{O}_2.$

Persulphuric acid, which is analogous to percarbonic acid, does not reduce a solution of a permanganate.

*Oxidation in Alkaline Solution.*—Many organic substances are oxidized by permanganates in alkaline solution with precipitation of manganese dioxide. Thus formic acid is oxidized to carbonic acid, ethyl alcohol to aldehyde and acetic acid, cellulose (paper) to oxalic acid principally, so that a solution of a permanganate cannot be filtered through paper. By boiling a concentrated

solution of potassium permanganate with concentrated potassium hydroxide, potassium manganate is formed with evolution of oxygen, and the color of the solution becomes green:



By heating solid potassium permanganate to  $240^\circ \text{C.}$ , potassium manganate is formed, also with evolution of oxygen:



**NICKEL**, Ni. At. Wt. 58.68.

Sp. Gr. = 8.9. M. Pt. =  $1450^\circ \text{C.}$

*Occurrence.*—In the native state nickel occurs only in meteorites. It is most frequently found in combination with sulphur, arsenic, and antimony in regular and hexagonal crystallizing minerals, of which the following are the most important:

**A. Isometric System.**

Chloanthite  
 $\text{NiAs}_2$ ;

Gersdorffite  
 $\text{NiAsS}$ ;

Ullmannite  
 $\text{NiSbS}$ .

**B. Hexagonal System.**

Niccolite  
 $\text{Ni}_2\text{As}_2$ ;

Breithauptite  
 $\text{Ni}_2\text{Sb}_2$ ;

Millerite  
 $\text{Ni}_2\text{S}_2$ .

Nickel also occurs as regular crystals of bunsenite,  $\text{NiO}$ , isomorphous with periclase,  $\text{MgO}$ , and manganosite,  $\text{MnO}$ ; as garnierite, or noumeite,  $\text{SiO}_4(\text{NiMg})\text{H}_2 + \text{aq}$ , a mineral occurring in New Caledonia, from which pure nickel can be prepared; and finally as annabergite,  $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , isomorphous with erythrite.

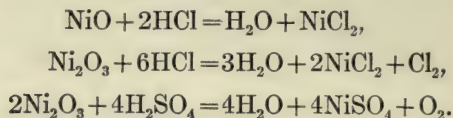
Metallic nickel possesses a silver-white color and is difficultly soluble in hydrochloric and sulphuric acids, but readily soluble in nitric acid. It forms two oxides:

Nickelous oxide,  $\text{NiO}$ .  
Green

Nickelic oxide,  $\text{Ni}_2\text{O}_3$ .  
Brownish black



By dissolving either of these oxides in acids, salts of bivalent nickel are always obtained:

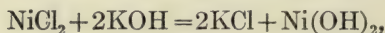


Nickelous oxide behaves as a basic anhydride, but nickelic oxide acts as a peroxide and forms no salts.

The crystallized salts of nickel and their aqueous solutions are green, but in the anhydrous condition they are usually yellow. Most of the salts are soluble in water; the sulphide, carbonate, and phosphate are insoluble.

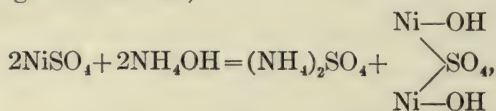
#### REACTIONS IN THE WET WAY.

1. **Potassium Hydroxide** precipitates apple-green nickelous hydroxide.



insoluble in excess of the precipitant, readily soluble in acids.

2. **Ammonia** precipitates (in neutral solutions free from ammonium salts) a green basic salt,



soluble (with a blue color) in excess of ammonia, forming a complex nickel ammonium salt:

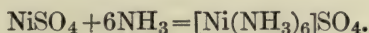
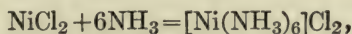


In the presence of sufficient ammonium salt ammonia produces no precipitate as with magnesium, ferrous and manganous salts; potassium and sodium hydroxides, however, precipitate the green hydroxide (difference from cobalt, see p. 156).

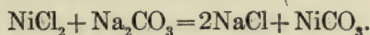
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\* Just as cyanogen possesses the ability to form with metals complex ions, so do ammonia, water, pyridine, etc. Cf. A. Werner, *Z. anorg. Chem.* 3 ff.; A. Werner and A. Miolatti, *Z. phys. Chem.* 12, 14, and 21.

The anhydrous chloride and sulphate readily absorb ammonia, forming anhydrous nickel ammonium salts:



3. **Potassium and Sodium Carbonates** precipitate apple-green nickel carbonate:

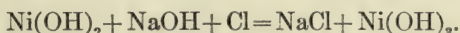


4. **Ammonium Carbonate** behaves similarly, only the precipitate which is formed is soluble in an excess of the precipitant, forming nickel ammonia carbonate.

5. **Sodium Hypochlorite** precipitates in the presence of alkalis all of the nickel as brownish-black nickelic hydroxide,  $\text{Ni}(\text{OH})_3$ . Nickelous hydroxide is first formed by the alkali present, but it is then oxidized by the hypochlorite to nickelic hydroxide:

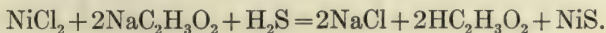


On adding chlorine or bromine to the nickel solution to which alkali has been added, nickelic hydroxide is likewise formed:

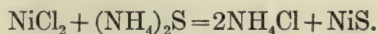


6. **Barium Carbonate** produces in the cold no precipitation; but by continued boiling, all of the nickel is thrown down as basic carbonate.

7. **Hydrogen Sulphide** precipitates no nickel from solutions which contain mineral acid or much acetic acid; but from solutions slightly acid with acetic acid and containing an alkali acetate, all the nickel is precipitated as the black sulphide:



8. **Ammonium Sulphide** precipitates from neutral solutions the nickel as sulphide:

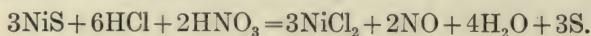


Nickel sulphide has a marked tendency to form colloidal solutions of a dark brown color, especially in the presence of am-

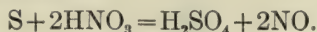
monia or a considerable excess of ammonium sulphide. By making the brown solution slightly acid with acetic acid and boiling, the hydrosol is coagulated and can be removed by filtration. The presence of ammonium salts also favors the coagulation of the hydrosol.

If it is desired to precipitate the nickel as sulphide from an ammoniacal solution, it is best to make the solution very slightly acid, add a little more ammonium chloride unless considerable is already present, heat to boiling, add colorless ammonium sulphide drop by drop until no further precipitation takes place, and then add 0.5 to 1 cc. of the reagent in excess. The nickel sulphide thus obtained can be filtered without difficulty and the filtrate is free from nickel. During the filtration care should be taken to keep the filter well filled with liquid to prevent the oxidation of the precipitate, which takes place readily on exposure to the air. To wash the precipitate it is well to use a hot, 5 to 10 per cent ammonium chloride solution to which a little colorless ammonium sulphide has been added. The washing can also be effected with hydrogen sulphide water without there being any danger of hydrosol formation.

Nickel sulphide is difficultly soluble in dilute mineral acids, readily soluble, however, in strong nitric acid or in aqua regia, with separation of sulphur:



The sulphur usually separates out as a black film. This is caused by the sulphur first melting in consequence of the heat of reaction, enclosing small particles of the black sulphide and protecting them from the action of the acid. By continued action of the acid all the sulphide is dissolved, and the sulphur remains as yellow drops, which are oxidized little by little to sulphuric acid, going into solution:

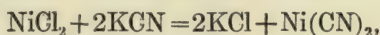


Nickel and cobalt sulphides, though not precipitated by hydrogen sulphide from a dilute, hydrochloric acid solution, dissolve with difficulty in a much stronger acid. This is probably caused by an abnormally slow rate of solution of the sulphides. Most schemes of qualitative analysis are based upon this behavior;

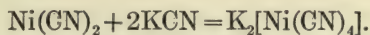


the nickel and cobalt are separated from zinc and manganese by treating the ammonium sulphide precipitate with cold, dilute hydrochloric acid. In such cases some nickel and cobalt always passes into solution and the quantity dissolved may be much larger than is ordinarily assumed. If the surface exposed to the action of the acid is large, or if left in a finely divided state by the dissolving out of other sulphide, a considerable quantity of nickel passes into solution in a comparatively short time. The reverse reaction, the precipitation of nickel sulphide by hydrogen sulphide in very dilute acid solution, also takes place very slowly but continuously. Cf. Noyes, Bray and Spear, J. Am. Chem. Soc. 1908.

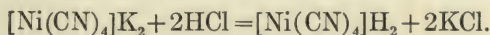
9. **Potassium Cyanide** produces a bright-green precipitate of nickelous cyanide:



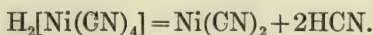
readily soluble in an excess of the precipitant, forming **potassium nickelocyanide**:



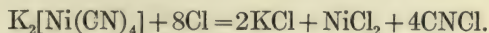
This last salt is readily decomposed by dilute mineral acids, with evolution of hydrogen cyanide and deposition of nickelous cyanide, which dissolves finally by the addition of more acid:



The nickelocyanic acid, which is first formed, is, like carbonic acid, very unstable, and decomposes according to the following equation:



Potassium nickelocyanide is not decomposed by ammonium sulphide (difference from manganese and zinc), but is readily decomposed by chlorine, bromine, and hypochlorites:



On adding sodium hydroxide to a solution of potassium nickelocyanide and conducting chlorine into the solution, nickelous chloride is first formed, which is decomposed by the caustic soda to nickel hydroxide; and the latter is oxidized by further action

of chlorine or bromine, forming black, voluminous nickelic hydroxide (cf. p. 149). This reaction is exceedingly delicate and serves for the detection of nickel in the presence of cobalt, as the corresponding complex cobalt cyanide compound is not decomposed under these conditions.

A large excess of potassium cyanide must be avoided, because in that case the reaction takes place much more slowly. The reaction depends entirely upon the presence in the solution of nickelous chloride, and this is formed only when the excess of the potassium cyanide has been destroyed. By the further action of chlorine the potassium nickelocyanide is decomposed; *i.e.*, nickel chloride is formed, upon which sodium hydroxide and chlorine act, forming black nickelic hydroxide.

The best procedure is as follows: A few drops of the solution to be tested for nickel are taken so that two or three drops of potassium cyanide will be sufficient to produce a clear solution, two to three cc. of double normal sodium hydroxide solution are added, and chlorine is conducted into the solution in the cold. Under these conditions a precipitate of  $\text{Ni(OH)}_2$  will be surely formed within one to two minutes.

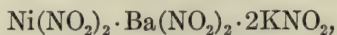
Bromine acts similarly to chlorine, but it is decidedly preferable to conduct chlorine gas into the solution.

10. **Sodium Phosphate** precipitates apple-green nickel phosphate,



readily soluble in acids, even acetic acid.

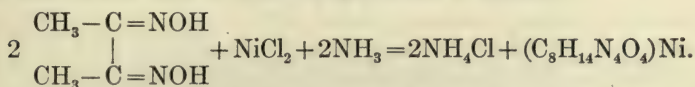
11. **Potassium Nitrite** produces in dilute nickel solutions no precipitate (difference from cobalt). In very concentrated solutions a brownish-red precipitate of  $\text{Ni(NO)}_2 \cdot 4\text{KNO}_2$  is thrown down; in the presence of alkaline earth salts a yellow crystalline precipitate is formed; *e.g.*,



which is very difficultly soluble in cold water, but readily soluble in boiling water, with a green color.

12. **Dimethylglyoxime**. If a little of this reagent is added to a solution of a nickel salt, then ammonia to slightly alkaline

reaction, and the solution is boiled, a red crystalline precipitate of the nickel salt of dimethylglyoxime is formed:



If the quantity of nickel present is very small, at first a yellowish solution is obtained from which, on cooling, red needles are deposited. According to L. Tschugaeff,\* who first proposed this qualitative test, the presence of one part of nickel can be detected in the presence of 400,000 parts of water. The reaction is not influenced by the presence of ten times as much cobalt; when a larger proportion of cobalt is present, the following procedure is followed.

### Detection of Traces of Nickel in Cobalt Salts.

The solution of the cobalt salt is treated with strong ammonia until a clear solution is obtained, then a few cubic centimeters of hydrogen peroxide are added and the solution boiled a few minutes to decompose the excess of this reagent. Then the dimethyl glyoxime is added and the solution is again brought to a boil. In the presence of very small quantities of nickel a red scum is formed and the glass sides of the beaker become coated with a film of red crystals. With smaller amounts of nickel the color is best observed upon the filter through which the solution is poured and the residue washed with hot water.

The above reaction is the most sensitive test we possess for detecting nickel in the presence of cobalt.

### REACTIONS IN THE DRY WAY.

The borax, or sodium metaphosphate, bead is brown in the oxidizing flame, almost the same shade as the strongly-saturated manganese bead; in the reducing flame the bead becomes gray, in consequence of the formation of some metallic nickel. On looking at the bead through the microscope the finely-divided metal can be seen suspended in the colorless glass.

On heating nickel salts with sodium carbonate on charcoal a

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\* Berichte, 38, 2520 (1905).



gray scale of metallic nickel is obtained. This reaction is best performed with the charcoal stick, as described on page 34. The magnetic metal obtained in this way is placed on a piece of filter-paper, dissolved in nitric acid, a drop of concentrated hydrochloric acid is added, and the paper carefully dried by moving it back and forth over the flame. If nickel is present the paper appears greenish (colorless with very small amounts of nickel), or bluish if cobalt is also present. The paper is now moistened (where the nickel is) with caustic soda or potash, and is then held in bromine vapors, which are obtained by shaking some bromine water in a wide-mouthed flask.

If nickel or cobalt is present, a black spot will be formed by the above treatment, consisting of the hydroxide of the trivalent metal (p. 149). The blackening often does not appear at first; in this case the paper is moistened once more with potassium hydroxide and again treated with bromine. The spot will now appear if nickel is present.

### COBALT, Co. At. Wt. 58.97.

Sp. Gr.=8.5. M. Pt.=1500°.

*Occurrence*—Like nickel, native cobalt is found only in meteorites. It occurs in the earth's crust chiefly as sulphide, arsenide, and as salts of sulphoarsenious and sulphoantimonous acids; it is almost always accompanied by nickel and iron.

The most important ores are smaltite,  $\text{CoAs}_2$ , isometric; cobaltite,  $\text{CoAsS}$ , isometric; skutterudite,  $\text{CoAs}_3$ , isometric; erythrite,  $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , monoclinic, isomorphous with vivianite,  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , and with annabergite,  $\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ .

Metallic cobalt is steel gray, dissolves much more readily in dilute acids than nickel, and is, like the latter, magnetic.

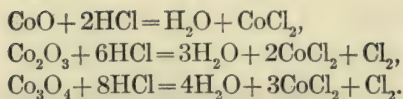
Cobalt forms, like iron, three oxides:

Cobaltous oxide  
 $\text{CoO}$ ,

Cobaltous cobaltic oxide  
 $\text{Co}_3\text{O}_4$ ,

Cobaltic oxide  
 $\text{Co}_2\text{O}_3$ .

By dissolving these three oxides in acids, salts derived from cobaltous oxide are always obtained, containing therefore bivalent cobalt:

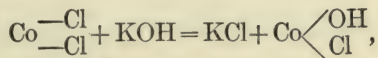


Simple cobaltic salts are unknown, but many complex compounds exist with trivalent cobalt, as, for example, potassium cobaltic nitrite, potassium cobaltic cyanide, and numerous cobaltic ammonium derivatives.

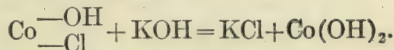
Cobaltous compounds in a crystallized state (as well as in aqueous solution) are pink, in the anhydrous condition yellow or green, and blue in aqueous solutions in the presence of hydrochloric acid. The solubility reactions of cobaltous salts are similar to those of manganese and nickel.

#### REACTIONS IN THE WET WAY.

1. **Potassium or Sodium Hydroxide precipitate in the cold a blue basic salt:**

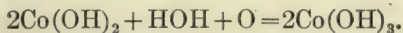


which on warming is further decomposed by potassium hydroxide, forming pink cobaltous hydroxide:



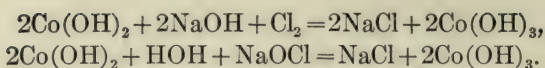
In the case of a moderately concentrated solution of the alkali the precipitate of pink cobaltous hydroxide is often produced in the cold, sometimes only after standing some time. The rapidity of the reaction depends entirely upon the concentration of the alkali.

Cobaltous hydroxide changes gradually to brown in contact with the air, going over into cobaltic hydroxide:



In this respect cobalt behaves similar to iron and manganese, and differs from nickel, for the hydroxide of the latter is not oxidized by atmospheric oxygen.

On adding chlorine, bromine, hypochlorites, hydrogen peroxide etc., to an alkaline solution containing cobaltous hydroxide, cobaltic hydroxide is immediately formed, as with nickel and manganese,



From ammoniacal cobalt solutions the above oxidizing agents cause no precipitation, but merely a red coloration; the addition of potassium hydroxide then causes no precipitation (difference from nickel).

*Remark.*—Cobaltous hydroxide,  $\text{Co}(\text{OH})_2$ , behaves under some conditions as a weak acid, for on adding to a cobaltous solution a very concentrated solution of KOH or NaOH the precipitate at first produced dissolves with a blue color \* similar to copper. By the addition of Rochelle salts to this blue cobalt solution the color either disappears almost entirely or becomes a pale pink, while the similarly treated copper solution becomes more intensely blue. By the addition of potassium cyanide to the blue cobalt solution it becomes yellow, and in contact with air turns intensely brown. A copper solution would be decolorized by the addition of potassium cyanide.

By pouring a little cobalt solution (or adding a little solid cobalt carbonate) into a concentrated solution of caustic soda or potash, to which a little glycerol has been added, a blue solution is formed (the color being intensified by warming), which after standing some time in the air, or immediately upon the addition of hydrogen peroxide, becomes a beautiful green.

2. **Ammonia** precipitates, in the absence of ammonium salts, a blue basic salt, soluble, however, in excess of ammonium chloride. Ammonia, therefore, produces no precipitate in solutions which contain sufficient ammonium chloride. The dirty yellow ammoniacal solution is little by little turned reddish on exposure to the air, owing to the formation of very stable cobaltic ammonium derivatives

3. **Alkali Carbonates** produce a reddish precipitate of basic salt of varying composition.

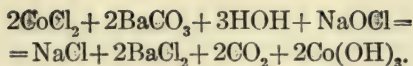
4. **Ammonium Carbonate** also precipitates a reddish basic salt, soluble, however, in excess.

5. **Barium Carbonate** precipitates in the cold, and in the absence of air, no cobalt; but on exposure to the air cobaltic hydroxide is gradually thrown down. The precipitation takes place much more quickly on the addition of hypochlorites or hydrogen peroxide:

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\* Ed. Donath, Z. anal. Chem., 40, p. 137 (1901).

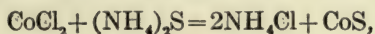




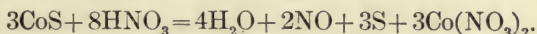
If the solution is heated to boiling, all of the cobalt is precipitated as a basic salt, even out of contact with the air.

6. **Hydrogen Sulphide** produces no precipitate in solutions containing mineral acids. In neutral solutions containing an alkali acetate all of the cobalt is precipitated as black sulphide.

7. **Ammonium Sulphide** precipitates black cobalt sulphide,



insoluble in ammonium sulphide, acetic acid, and very dilute hydrochloric acid;\* soluble in concentrated nitric acid and aqua regia, with separation of sulphur:



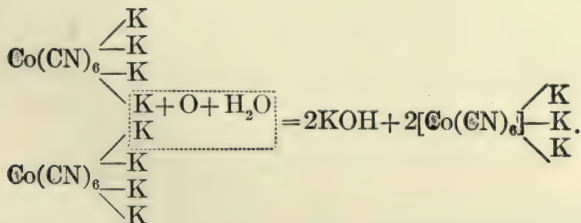
By continued action of strong nitric acid all the sulphur goes into solution.

8. **Potassium Cyanide** produces in neutral solutions a reddish-brown precipitate, soluble in excess of potassium cyanide in the cold, with a brown color, forming potassium cobaltocyanide:



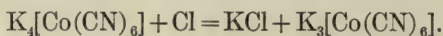
On warming the brown neutral solution for some time it becomes a bright yellow and reacts alkaline; it now contains potassium cobalticyanide, of analogous composition to potassium ferri-cyanide.

The formation of the cobaltic salt takes place with the help of atmospheric oxygen:



\* Cf. page 151.

The reaction takes place more quickly by means of chlorine, bromine, hypochlorites, etc.:



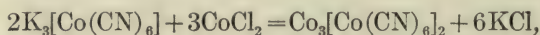
An excess of chlorine, bromine, etc., does not decompose the cobaltic salt (difference from nickel).

Potassium cobalticyanide is very much more stable than the cobaltous compound. By adding hydrochloric acid to the brown solution of potassium cobaltocyanide, hydrogen cyanide will be set free and yellow cobaltous cyanide formed,



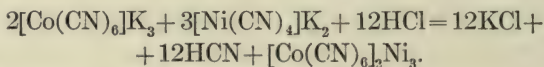
while potassium cobalticyanide is not decomposed by hydrochloric acid.

Potassium cobalticyanide forms, with most of the heavy metals, difficultly soluble or insoluble salts possessing characteristic colors. Thus, it produces with cobaltous salts pinkish-red cobaltous cobalticyanide:



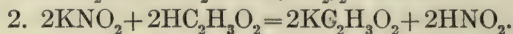
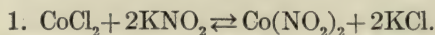
and with nickel salts greenish nickelous cobalticyanide.

If, therefore, a cobalt solution contains nickel it gives, on precipitating and redissolving with potassium cyanide, boiling, and adding hydrochloric acid, a greenish precipitate of nickelous cobalticyanide:

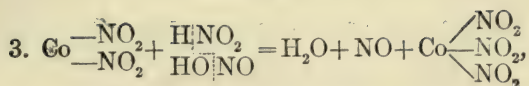


**9. Potassium Nitrite** produces in concentrated solutions of cobalt salts, with the addition of acetic acid, an immediate precipitation of yellow crystalline potassium cobaltic nitrite. If the solution is dilute, the precipitate appears only after standing for some time, but more quickly on rubbing the sides of the beaker.

The reaction takes place in the following stages:



The free nitrous acid oxidizes the cobaltous nitrite to cobaltic nitrite,

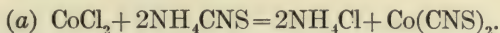


which now combines with more potassium nitrite:



This reaction offers an excellent means for detecting the presence of cobalt in nickel salts.

10. **Ammonium Sulphocyanate** (Vogel's reaction).\* If a concentrated solution of ammonium sulphocyanate is added to a cobaltous solution, the latter becomes a beautiful blue, owing to the formation of ammonium cobaltous sulphocyanate:



On adding water the blue color disappears and the pink color of the cobaltous salt takes its place. If, now, amyl alcohol † is added (or a mixture of equal parts amyl alcohol and ether), and the solution shaken, the upper alcoholic layer is colored blue. This reaction is so sensitive that the blue color is recognizable when the solution contains only  $\frac{2}{1000}$  of a milligram of cobalt. The blue solution also shows a characteristic absorption spectrum.‡ Nickel salts produce no coloration of the amyl alcohol. If, however, iron is present, the red  $\text{Fe}(\text{CNS})_3$  is formed, which likewise colors the amyl alcohol, making the blue color (due to the cobalt) very indistinct, so that, under some conditions, it can no longer be detected. If, however, some sodium carbonate solution is added drop by drop, the iron will be precipitated as ferric hydroxide, while the blue color produced by the cobalt is unaffected.

\* Ber. 12, 2314 Treadwell, Z. anorg. Chem. 26, 105 (1901).

† T. T. Morrell first showed that cobalt salts give a blue color with ammonium sulphocyanate, disappearing on the addition of water, but reappearing when alcohol is added. Z. anal. Chem. 16, 251.

‡ Wolff, Z. anal. Chem. 18, 58.



**Detection of Traces of Cobalt in Nickel Salts.**

In order to test a nickel salt for cobalt, a concentrated solution of ammonium sulphocyanate is added to the solution of a considerable amount of the salt, a few cubic centimeters of a mixture of amyl alcohol and ether are added and the solution shaken. After the latter has been allowed to settle, if the upper alcohol-ether layer is colorless, then the nickel salt contains neither iron nor cobalt; if the layer is reddish, iron is present. In this case a few drops of dilute sodium carbonate solution\* are added, and the solution again shaken; if cobalt is present the alcohol-ether layer is now distinctly blue.

**REACTIONS IN THE DRY WAY.**

The bead produced by borax or sodium metaphosphate is blue in both the oxidizing and reducing flames. By holding the bead in the upper reducing flame for a long time it is possible to reduce the cobalt to metal, when it appears, like nickel, gray.

On the charcoal stick cobalt compounds yield gray metallic cobalt, which can be removed by means of a magnetized knife-blade, as described on page 35, placed on filter-paper, dissolved in hydrochloric acid and dried. The paper is then colored blue by cobalt (difference from nickel). If, now, sodium hydroxide is added and the paper exposed to the action of bromine vapors, black cobaltic hydroxide,  $\text{Co}(\text{OH})_3$ , is formed.

**ZINC, Zn. At. Wt. 65.37.**

Sp. Gr.=6.9. M. Pt.=419° C. B. Pt.=930° C.

*Occurrence.*—Smithsonite,  $\text{ZnCO}_3$ , isomorphous with calcite,  $\text{CaCO}_3$ , etc.; sphalerite,  $\text{ZnS}$ , isometric; calamine,  $\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$ , orthorhombic, hemimorphic; zincite,  $\text{ZnO}$ , hexagonal; and franklinite,  $(\text{FeO}_2)_2(\text{Fe}, \text{Mn}, \text{Zn})$ , isometric.

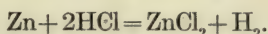
The most important zinc ore is sphalerite,  $\text{ZnS}$ . Sulphide of zinc is dimorphic and is also found as wurtzite which crystallizes in the hexagonal system.

Metallic zinc is bluish white. At low temperatures and at about 200° C. it is so brittle that it can be pulverized, but at 110°–150° C. it is ductile and can be drawn out into wire and rolled into foil.

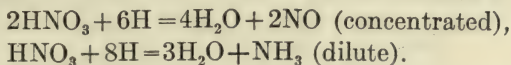
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\* It is better to add a few drops of Rochelle salt solution.

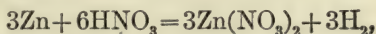
Zinc is readily soluble in all acids; in hydrochloric, sulphuric, and acetic acids with evolution of hydrogen:



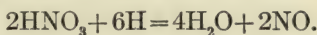
Nitric acid dissolves it forming the nitrate, but hydrogen is not evolved on account of its being used up in reducing the excess of nitric acid. The reduction products are different according to the concentration of the acid used; with concentrated acid, nitric oxide, NO, is formed, while dilute acid is reduced to ammonia:



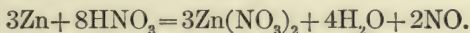
The solution of zinc in *concentrated* nitric acid may be supposed to take place as follows: First of all, the nitrate is formed, with evolution of hydrogen,



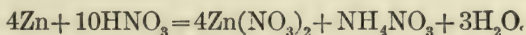
and the latter is used up as quickly as it is formed by reducing the nitric acid to nitric oxide:



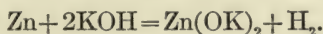
The whole reaction, then, may be represented by the equation



A similar reaction takes place in the solution of zinc in *dilute* nitric acid:

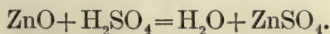


Like aluminium zinc dissolves in caustic soda or potash, with evolution of hydrogen and the formation of a zincate:



Zinc forms only one oxide, ZnO. It is a white infusible powder, which becomes yellow when heated, but turns white again on cooling.

Zinc oxide dissolves readily in acids, forming zinc salts:

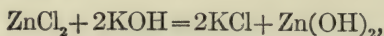


There exists only one series of zinc salts, and the zinc is always

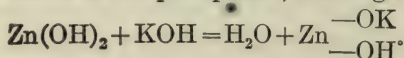
bivalent. Most of the salts are white. The chloride, nitrate, sulphate, and acetate are soluble in water; the remainder dissolve readily in mineral acids.

#### REACTIONS IN THE WET WAY.

1. **Potassium and Sodium Hydrates** precipitate white gelatinous zinc hydroxide.



easily soluble in excess of the precipitant, forming a zincate:\*



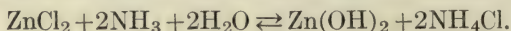
Zinc hydroxide, therefore, behaves sometimes as a base and sometimes as an acid, like aluminium hydroxide.

On boiling a diluted solution of a zincate, hydrolysis takes place and zinc hydroxide is precipitated:

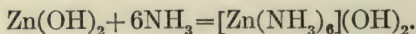


If, however, the solution contains considerable sodium or potassium hydroxide, there will be no precipitation.

2. **Ammonia** precipitates from neutral solutions, free from ammonium salts, zinc hydroxide, readily soluble in ammonium salts, as in the case of magnesium, nickel, manganese, or iron:



Zinc hydroxide is also soluble in an excess of ammonia, due to the formation of complex zinc ammonium hydroxide:



\* According to Hantzsch the zinc is not present as zincate, but probably as hydroxide in the hydrosol form. *Z. anorg. Chem.* **30**, p. 289 (1902). In fairly concentrated solutions, however, it is certain that the zinc is present as zincate, for F. Foerster and O. Günther have isolated the compound,  $\text{Zn} \begin{array}{c} \text{ONa} \\ \text{OH} \end{array} + 3\text{H}_2\text{O}$ , as needles with silky luster. *Z. Electrochem.* **6**, 301 (1900).



In the presence of ammonium salts the corresponding salt is formed:

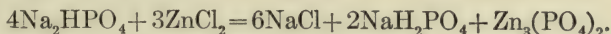


3. **Alkali Carbonates** precipitate a white, basic carbonate, of variable composition, as is the case with magnesium (p. 65).

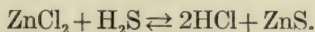
4. **Ammonium Carbonate** does the same, except that the precipitate is soluble in an excess of the reagent. The presence of ammonium salts prevents the precipitation.

5. **Barium Carbonate** precipitates no zinc in the cold, but on boiling all the zinc is precipitated as basic carbonate.

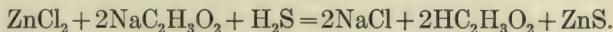
6. **Sodium Phosphate** precipitates gelatinous, tertiary zinc phosphate, which soon becomes crystalline, and is soluble in ammonia and in acids:



7. **Hydrogen Sulphide** precipitates, from neutral solutions of a zinc salt of a mineral acid, the zinc incompletely as sulphide:

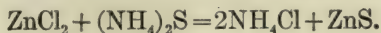


Zinc sulphide is soluble in mineral acids; consequently the above reaction is reversible. The more dilute the solution, the more complete will be the precipitation; but it will never be quantitative. Zinc sulphide is insoluble in acetic acid. If, therefore, we add some sodium acetate to the solution, and then introduce hydrogen sulphide, all the zinc will be thrown down as sulphide:



The solution of zinc sulphide in acids requires the presence of hydrogen ions. When hydrogen sulphide is passed into an aqueous solution of zinc chloride, the concentration of hydrogen ions increases as the zinc sulphide is formed and soon suffices to stop the precipitation. Sodium acetate reacts with these hydrogen ions to form undissociated acetic acid. Acetic acid is too slightly dissociated to stop the precipitation.

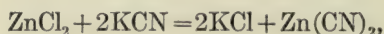
8. **Ammonium Sulphide** precipitates from neutral or alkaline solutions all the zinc as amorphous sulphide:



Zinc sulphide is a precipitate hard to filter; it runs through the filter-paper, particularly on washing. This is a peculiarity of almost all metallic sulphides and of many other amorphous bodies, such as aluminium hydroxide, titanac acid, tungstic acid, and many others. Such bodies exist in a soluble form as hydrosol, and in an insoluble form as hydrogel. The hydrosol can be changed into hydrogel by precipitation with concentrated salt solutions, or by boiling, or by the addition of acids.

In order, then, to obtain zinc sulphide in a form which can be filtered, it is best precipitated from a boiling solution containing acetic acid and considerable amount of ammonium salts.\* The precipitate may be washed with a solution of ammonium chloride to which a little ammonium sulphide has been added.

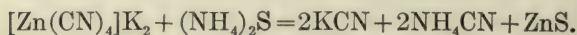
9. **Potassium Cyanide** produces a white precipitate of zinc cyanide, soluble in an excess of the precipitant.



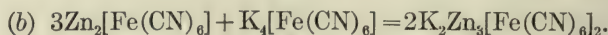
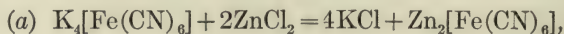
and



Zinc potassium cyanide is readily decomposed by acids and alkali sulphides:



10. **Potassium Ferrocyanide** precipitates white zinc ferrocyanide, which is changed by an excess of the potassium ferrocyanide into insoluble zinc potassium ferrocyanide:




---

\* In separating iron from zinc by hydrogen sulphide it has been found advisable to use a stronger acid than acetic acid. Thus formic acid and ammonium formate have been used.

The formation of the last-named body plays an important part in the volumetric determination of zinc, according to the method of Galetti.

#### REACTIONS IN THE DRY WAY.

Heated with sodium carbonate on charcoal before the blowpipe, it is not possible to obtain metallic zinc on account of its volatility; but an incrustation of oxide is obtained which is yellow while hot and white when cold.

Zinc oxide (or such compounds of zinc as are changed over to oxide on ignition), when moistened with cobalt nitrate yields a green infusible mass: Rinnmann's green. This reaction is performed exactly as with aluminium (p. 95).

#### Separation of the Metals of Group III from the Alkalies and Alkaline Earths.

The separation of the members of the ammonium sulphide group from the alkalies and alkaline earths is effected by means of ammonium sulphide and ammonium chloride. If, however, the solution contains phosphoric acid, oxalic acid, or considerable boric acid, ammonia and ammonium sulphide will each precipitate calcium, strontium, barium, and magnesium as phosphate, oxalate, or borate together with the members of the ammonium sulphide group. This special case will be treated in Part II.

*The separation of the metals of Group III is effected according to Tables II, III and IV, pages 166, 167, and 168.*



TABLE II. SEPARATION OF MANGANESE, NICKEL, COBALT, AND ZINC.

The solution containing ammonium chloride is treated with ammonia until alkaline, and hydrogen sulphide is passed in until it becomes saturated. The precipitate is filtered off and washed three times with water to which a little ammonium sulphide has been added. The precipitate is then removed to a porcelain dish and treated with cold double-normal hydrochloric acid, being stirred with a glass rod until no more hydrogen sulphide is given off, when it is filtered.

RESIDUE ( $\text{CoS}, \text{NiS}$ ).SOLUTION ( $\text{MnCl}_2, \text{ZnCl}_2$ , and traces of  $\text{NiCl}_2$ ).

The residue is tested for cobalt by heating a small portion with the borax bead; a blue bead shows cobalt.

In order to test for nickel, a portion is dissolved in a few drops of aqua regia, evaporated just to dryness, and dissolved in a little water; potassium cyanide is added drop by drop until the precipitate produced is entirely dissolved, two to three c.c. of sodium hydroxide are added and chlorine conducted into the cold solution. If nickel is present, black  $\text{Ni}(\text{OH})_3$  is formed within a few minutes.

The dimethylglyoxime test for nickel is more sensitive. See page 153.

N.B.—If the borax bead was brown in the cobalt test, a further test for nickel is unnecessary. Very small amounts of cobalt may be present. In order to detect the cobalt, a considerable amount of the precipitate is dissolved in aqua regia, evaporated just to dryness, dissolved in as little water as possible, a concentrated solution of potassium nitrite is added, the solution is acidified with acetic acid and allowed to stand twelve hours. A yellow crystalline precipitate of  $[\text{Co}(\text{NO}_2)_2]_3$  shows cobalt to be present (cf. p. 158).

Vogel's reaction (p. 159) is still better for detecting small amounts of cobalt. For this purpose the aqueous solution, obtained as before, is treated with a concentrated solution of  $\text{NH}_4\text{SCN}$  and shaken with a few c.c. of a mixture of equal parts amyl alcohol and ether. If the upper layer of alcohol-ether solution is colored blue, cobalt is present.

The solution is boiled until hydrogen sulphide ceases to be given off, then precipitated with strong caustic potash and filtered.

PRECIPITATE  $[\text{Mn}(\text{OH})_2$  and a little  $\text{Ni}(\text{OH})_2]$ . SOLUTION  $[\text{Zn}(\text{OK})_2]$ .

(a) A portion of the precipitate is dissolved in a little hydrochloric acid, evaporated carefully to dryness, and dissolved in a little water; a few drops of potassium cyanide solution are added; the solution is diluted largely with water, treated with  $(\text{NH}_4)_2\text{S}$  and boiled.

A flesh-colored precipitate of  $\text{MnS}$  shows manganese.

(b) A small portion of the precipitate is dissolved in concentrated nitric acid and a knife-blade of lead peroxide is added; the mixture is then boiled and diluted with water.

The supernatant solution is colored red if manganese is present.

(c) A small portion of the precipitate is fused on platinum foil with sodium carbonate and potassium carbonate.

The melt is colored green if manganese is present.

On dissolving in a little water, and acidifying with a few drops of acetic acid, a red solution is obtained.

The solution is acidified with acetic acid, and hydrogen sulphide is passed into the solution.

A white precipitate of  $\text{ZnS}$  shows zinc.

The precipitate is filtered, a small portion is transferred to a piece of filter-paper and placed in a platinum spiral. It is then treated with nitric acid, evaporated to dryness, moistened with dilute cobalt nitrate solution and ignited.

A green infusible mass (Rinnmann's green) shows zinc.

TABLE III. FIRST METHOD OF SEPARATING ALL THE MEMBERS OF THE AMMONIUM SULPHIDE GROUP.

(To be used in the presence of considerable cobalt.)

The neutral solution, which should contain ammonium chloride, is treated at the boiling temperature with ammonium sulphide added drop by drop until no further precipitation takes place; or it is treated with ammonia in excess and saturated with hydrogen sulphide. The precipitate, which consists of  $\text{Fe}_2\text{S}_3$ ,  $\text{FeS}$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{UO}_2\text{S}$ ,  $\text{MnS}$ ,  $\text{NiS}$ ,  $\text{CoS}$ , and  $\text{ZnS}$ , is filtered off and washed. It is then treated with cold double-normal hydrochloric acid in a porcelain dish, being stirred until no more hydrogen sulphide is given off, when it is filtered.

A. RESIDUE  $[\text{CoS}, \text{NiS}]$ . B. SOLUTION  $[\text{FeCl}_3, \text{UO}_2\text{Cl}_2, \text{AlCl}_3, \text{CrCl}_3, \text{MnCl}_2, \text{ZnCl}_2, \text{(traces of NiCl}_2\text{)}]$ .

To be examined by Table II.

The solution is evaporated to a small volume, oxidized with two to three c.c. of concentrated nitric acid, treated with concentrated sodium hydroxide until strongly alkaline, boiled and filtered.  
C. PRECIPITATE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{U}_2\text{O}_7\text{N}_2, \text{Mn}(\text{OH})_2, \text{Ni}(\text{OH})_2]$ . D. SOLUTION  $[\text{AlO}_2\text{Na}, \text{Zn}(\text{ONa})_2]$ .

The precipitate is dissolved in as little concentrated hydrochloric acid as possible, diluted with a little hot water, and boiled several minutes. Ammonium chloride is added, the boiling solution treated with a slight excess of ammonia and filtered as quickly as possible.

E. PRECIPITATE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{(NH}_4\text{)}_2\text{U}_2\text{O}_7]$ . F. SOLUTION  $\text{MnCl}_2$  and traces of  $\text{NiCl}_2$ .

The precipitate is dissolved in as little concentrated  $\text{HCl}$  as possible, treated with a large excess of ammonium carbonate, warmed slightly (*should not be boiled long!*), and filtered.

I. PRECIPITATE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3]$ . J. SOLUTION  $[\text{UO}_2(\text{CO}_3)_2(\text{NH}_4)_2]$ .

Iron and chromium are tested for according to Table I.

Uranium is tested for according to Table I.

The solution is acidified with hydrochloric acid, an excess of ammonia is added, and the solution filtered.

G. PRECIPITATE  $[\text{Al}(\text{OH})_3]$ . H. SOLUTION  $[\text{Zn}(\text{NH}_3)_6\text{Cl}_2]$ .

A white gelatinous precipitate shows the presence of aluminium. It is confirmed by the Thénard's blue reaction (p. 95).

The solution is acidified with acetic acid and hydrogen sulphide passed into it. A white precipitate of  $\text{ZnS}$  shows zinc. It is confirmed by the Rinnmann's green reaction (Table II).

TABLE IV. SECOND METHOD OF SEPARATING ALL THE MEMBERS OF THE AMMONIUM SULPHIDE GROUP.

(To be used when no cobalt is present, or only a small amount.)

The metals are assumed to be present as chlorides. The iron is oxidized by means of nitric acid,\* and the solution boiled for some time to expel all free chlorine; † 20 c.c.  $\text{NH}_4\text{Cl}$  solution are added; the solution is precipitated at the boiling temperature by as little ammonia as possible and filtered quickly.

A. PRECIPITATE  $[\text{Fe}(\text{OH})_3, \text{Al}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{U}_2\text{O}_7(\text{NH}_4)_2] \ddagger$

The precipitate is dissolved in as little concentrated  $\text{HCl}$  as possible, filtered with a little water, precipitated with an excess of  $\text{NaOH}$  and filtered red.

C. PRECIPITATE  $[\text{Cr}(\text{OH})_3, \text{Co}(\text{OH})_2]$

D. SOLUTION  $[\text{Al}(\text{ONa})_3]$ .

Examined according to Table III, E.

Acidified with  $\text{HCl}$  and precipitated with ammonia; a white gelatinous precipitate shows aluminium.  
Confirm by Thénard's blue reaction (see page 95).

B. SOLUTION  $[\text{MnCl}_2, \text{ZnCl}_2, \text{NiCl}_2, \text{CoCl}_2]$ .

The solution is precipitated with colorless ammonium sulphide and filtered.

E. PRECIPITATE  $[\text{MnS}, \text{ZnS}, \text{NiS}, \text{CoS}]$  F. SOLUTION.

Examined according to Table II.

Contains members of the following groups.

\* The solution should be tested, to see if all of the ferrous iron has been oxidized, by adding a drop of the solution to a drop of potassium ferricyanide on the cover of a porcelain crucible. There should be no trace of Turnbull's blue apparent.  
† Free chlorine is formed by the action of nitric acid upon hydrochloric acid or upon the chlorides present. If it is not expelled, manganese, nickel, and cobalt will be precipitated as  $\text{Mn} \begin{smallmatrix} \text{OH} \\ \diagup \text{O} \diagdown \\ \text{OH} \end{smallmatrix}$ ,  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$ .

‡ If considerable manganese is present, some will always be carried down with this precipitate. It is, therefore, advisable to dissolve the precipitate produced by ammonia in hydrochloric acid and repeat the precipitation with ammonia. The filtrate from the second precipitation is added to B.  
Cobalt acts still worse than manganese. If considerable cobalt is present, even four repeated precipitations with ammonia are insufficient to completely separate the cobalt from the iron, because the ammoniacal solution absorbs oxygen rapidly, precipitating the cobalt as  $\text{Co}(\text{OH})_3$ . In this case it is always better to effect the separation according to Table III.

Zinc, in the presence of considerable chromium, is likely to follow the latter element in the above scheme of analysis. It is advisable, therefore, to test a part of the sodium hydroxide precipitate obtained at C for zinc. It is dissolved in dilute hydrochloric acid and the solution is neutralized with ammonia, acidified with acetic acid and saturated with hydrogen sulphide. A white precipitate is confirmed as under H in Table III.



## METALS OF GROUP II. HYDROGEN SULPHIDE GROUP.

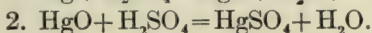
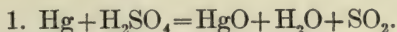
**MERCURY, LEAD, COPPER, BISMUTH, CADMIUM, ARSENIC, ANTIMONY, TIN (GOLD, PLATINUM, SELENIUM, TELLURIUM, VANADIUM, TUNGSTEN, MOLYBDENUM, THALLIUM).**

**MERCURY, Hg. At.Wt. 200.6.**

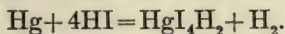
Sp. Gr.=13.595. M. Pt.= $-39.4^{\circ}$  C. B. Pt.= $357^{\circ}$  C.

*Occurrence.*—Mercury occurs in nature chiefly in the form of rhombohedral cinnabar,  $\text{HgS}$ ; from the ore, free mercury is obtained by sublimation. According to G. F. Becker,\* cinnabar is deposited from solutions of its sulpho salt. The richest deposits are those of New Almaden in California, where it occurs with serpentine; of Almaden in Spain, Idria in Carniola, and Moschellandsberg in the Palatinate of the Rhine. With the cinnabar small amounts of native mercury are often found. Mercury is also an important constituent of many varieties of tetrahedrite.

Metallic mercury is the only one of the metals which is liquid at ordinary temperatures. It is insoluble in hydrochloric and dilute sulphuric acids, but is soluble in hot concentrated sulphuric acid with evolution of sulphur dioxide, forming mercurous or mercuric sulphate according to whether the metal or the acid is present in excess. The formation of mercuric sulphate takes place according to the equations



Hydrobromic acid hardly attacks the metal at all, while in hydriodic acid the metal dissolves readily with evolution of hydrogen:

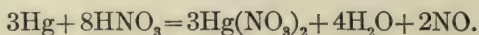


*The proper solvent for mercury is nitric acid.*

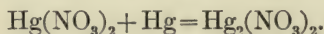
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\* Geology of the Quicksilver Deposits of the Pacific Slope. Washington, 1888.

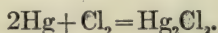
If the metal is treated with hot concentrated nitric acid, mercuric nitrate is formed:



If, however, cold nitric acid is allowed to act upon an excess of mercury in the cold, mercurous nitrate is obtained:



Mercury is attacked by chlorine, forming calomel (mercurous chloride):



Two oxides of mercury are known:

1. Yellow or red mercuric oxide,  $\text{HgO}$ .
2. Black mercurous oxide,  $\text{Hg}_2\text{O}$ .

These oxides are basic anhydrides, from which two series of salts are derived:

- (a) The mercuric salts, which contain the group  $\text{Hg} <$ , and
- (b) the mercurous salts, which contain the group  $\text{Hg} -$



We will consider first the more stable mercuric salts.

### Mercuric Salts.

Mercuric salts are mostly colorless. The iodide is red or yellow. By heating the red tetragonal crystals of mercuric iodide a yellow sublimate of orthorhombic needles is obtained, which gradually changes back to the red tetragonal modification; very quickly, almost instantly, if the yellow crystals are rubbed. This is a general property of dimorphous bodies; *the more symmetrical form is almost always the more stable.*

The sulphide is black or red.

Mercuric chloride is soluble in water, 100 parts of water dissolving at

10°	20°	50°	80°	100°
6.57	7.39	11.34	24.3	53.96

grams  $\text{HgCl}_2$ .

In water containing hydrochloric acid, mercuric chloride is much more soluble than in pure water; and in fact the solubility in-

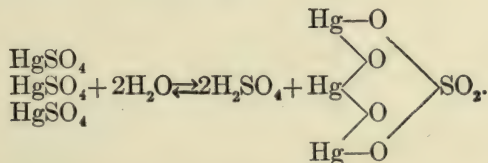
creases with the concentration of the hydrochloric acid, probably due to the formation of the complex acid  $(\text{HgCl}_4)\text{H}_2$ .

The aqueous solution of mercuric chloride is a poor conductor of electricity; it is only dissociated to a slight extent and acts quite differently in many cases from a solution of the nitrate, which is a good conductor of electricity and therefore contains a good many mercuric ions. The cyanide differs from the nitrate even more, as we shall see.

Mercuric bromide is difficultly soluble in water (94 parts of water dissolve at 9° C. only 1 part of the bromide), but is readily soluble in alcohol, and still more soluble in ether. The iodide is more difficultly soluble.

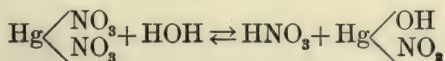
The halogen compounds of mercury readily form complex compounds with the halogen compounds of the alkalis, which are very stable.

Mercury compounds are furthermore characterized by the readiness with which they undergo hydrolysis, forming insoluble basic salts. Thus the sulphate is decomposed when diluted largely with water (particularly on warming) into a yellow insoluble basic salt:

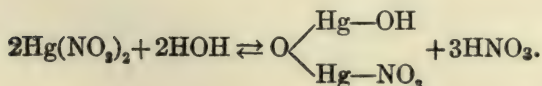


The basic sulphate dissolves readily in hydrochloric acid.

The nitrate also is readily hydrolyzed into more or less insoluble basic salts according to the "mass action" of the water. The neutral salt forms with water a basic salt according to the equation



or

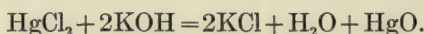




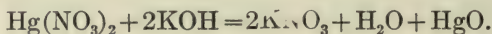
## REACTIONS IN THE WET WAY.

A solution of mercuric chloride and one of mercuric nitrate are used for these reactions.

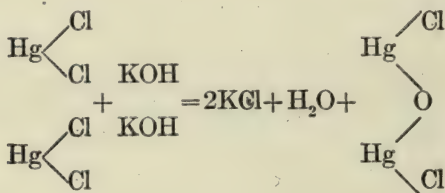
1. **Potassium Hydroxide** precipitates yellow mercuric oxide:



The hydroxides of the noble metals are exceedingly unstable; they lose water, as a rule, even in aqueous solution, forming the anhydrous oxide.



On adding a lesser amount of caustic potash to a solution of mercuric chloride, a reddish-brown precipitate of basic chloride is obtained.

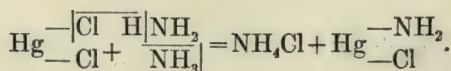


or



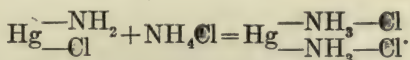
The mercuric oxide and the basic salts are readily soluble in acids.

2. **Ammonia** produces in a solution of mercuric chloride a white precipitate of mercuric aminochloride:

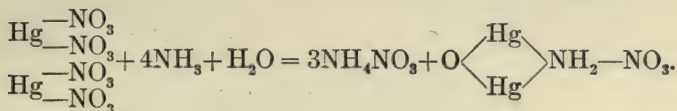


This compound, the so-called "infusible precipitate," volatilizes

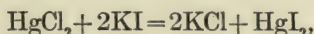
before it melts. It is soluble in acids, and in hot ammonium chloride, forming the "fusible precipitate"



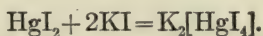
If ammonia is allowed to act upon mercuric nitrate a white oxyamino compound is always formed:



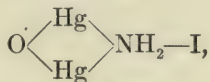
3. **Potassium Iodide** produces a red precipitate of mercuric iodide,



soluble in excess of potassium iodide, forming a colorless complex salt:

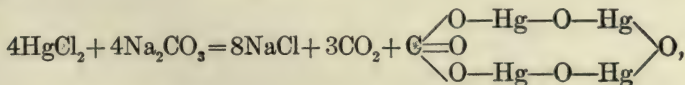


The solution of the latter salt contains no mercuric ions, for it gives no precipitate with caustic soda or potash. The alkaline solution is the so-called "Nessler's reagent," and serves for the detection of very slight traces of ammonia. There is formed in this reaction the brown-colored compound



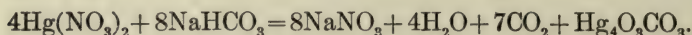
which is soluble in an excess of the "Nessler's reagent," with an intense yellow color (cf. p. 58).

4. **Alkali Carbonates** precipitate from both the chloride and the nitrate a reddish-brown basic carbonate in the cold,

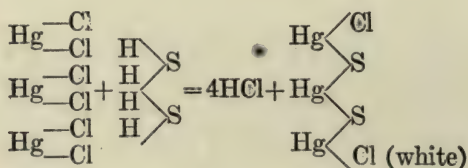


which on boiling loses carbon dioxide and is changed into yellow mercuric oxide.

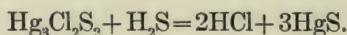
5. **Alkali Bicarbonates** produce no precipitation in a solution of mercuric chloride, but do cause precipitation from mercuric nitrate:



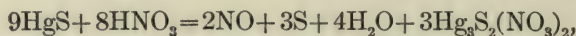
6. **Hydrogen Sulphide** produces in solutions of mercuric salts a precipitate which is at first white, then yellow, brown, and finally black. The white precipitate is formed according to the following equation;



By the further action of hydrogen sulphide, black mercuric sulphide is finally obtained:

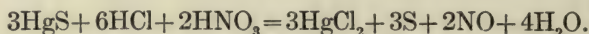


Mercuric sulphide is insoluble in dilute boiling acids. Hot concentrated nitric acid transforms it gradually into white  $\text{Hg}_3\text{S}_2(\text{NO}_3)_2$ ,

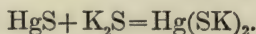


which by long boiling is changed into the soluble nitrate.

It dissolves readily in aqua regia, forming the chloride with separation of sulphur:



Mercuric sulphide is insoluble in caustic soda and potash solutions, and in ammonium sulphide, but it dissolves readily in sodium or potassium sulphide:



By dilution with water this compound is completely hydrolyzed into mercuric sulphide and potassium hydroxide:



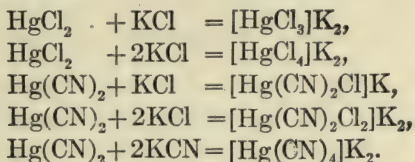
Therefore it is always necessary to dissolve the mercuric sulphide with considerable potassium sulphide, or with little potassium sul-



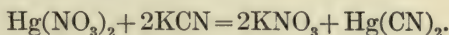
phide and considerable caustic potash, in order to prevent this hydrolysis.

The fact that  $\text{Hg}(\text{SK})_2$  is so readily hydrolyzed explains the formation of cinnabar in nature. In the interior of the earth the sulpho-compound is formed, which is brought by springs to the surface and there undergoes the above decomposition.

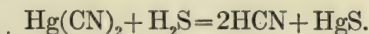
**7. Potassium Cyanide** produces in a solution of mercuric chloride no precipitation, because the cyanide, as well as the chloride, forms readily soluble complex compounds with alkali chlorides. The following are known:



In a concentrated solution of mercuric nitrate, potassium cyanide produces a precipitate of mercuric cyanide, soluble in considerable water and in potassium cyanide:



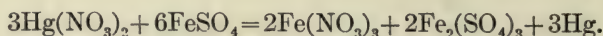
Mercuric cyanide is the only cyanide of the heavy metals that is soluble in water. It dissolves mercuric oxide perceptibly, forming the complex compound  $(\text{HgCN})_2\text{O}$ . Mercuric cyanide is not precipitated by alkali carbonates or by caustic alkalies, because the mercuric oxide is soluble in mercuric cyanide. It is not decomposed by dilute sulphuric acid, although it is by the halogen acids—most difficultly by hydrochloric acid, and most readily by hydriodic acid; hydrogen sulphide decomposes it with precipitation of mercuric sulphide:



**8. Neutral Alkali Chromates** precipitate yellow mercuric chromate from both the chloride and nitrate solutions. On long standing or by boiling, the precipitate becomes red; a basic salt being probably formed.

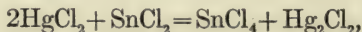
**9. Alkali Dichromates** throw down a yellowish-brown precipitate from the nitrate solution, but not from that of the chloride.

10. **Ferrous Sulphate** reduces mercuric nitrate on boiling to metallic mercury:

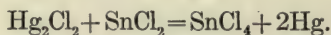


Mercuric chloride and cyanide are not reduced by ferrous sulphate.

11. **Stannous Chloride** reduces mercuric salts, at first to insoluble mercurous chloride (calomel),

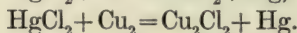
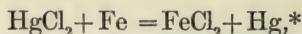


and by further action to metal,



Metallic mercury separates out in the form of a gray powder. By decanting the solution, and boiling the residue with dilute hydrochloric acid, the mercury appears in tiny globules.

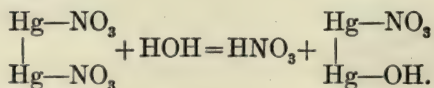
12. **Copper, Zinc, and Iron** precipitate mercury from solutions of its salts:



On placing a drop of mercury solution (whether of a mercurous or a mercuric salt) upon a piece of bright copper-foil, a gray spot is formed, which, after being dried, becomes bright as silver on rubbing.

### Mercurous Salts.

The mercurous salts all contain the bivalent mercurous group  $\begin{array}{c} \text{Hg—} \\ | \\ \text{Hg—} \end{array}$  and are changed more or less readily into mercuric salts, splitting off one atom of mercury from the molecule. Mercurous salts containing oxygen, like mercuric salts, are readily hydrolyzed in dilute aqueous solutions; thus the nitrate is decomposed according to the equation



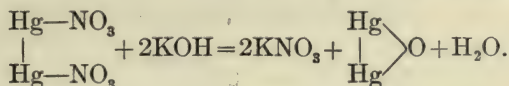

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\* This reaction is employed for detecting metallic iron in the presence of FeO (cf. p. 116).

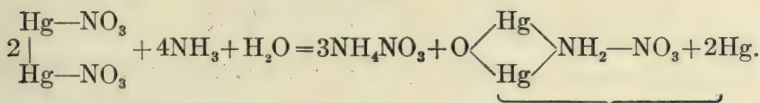
Mercurous chloride (calomel) is insoluble in water and hydrochloric acid, but soluble in nitric acid and aqua regia.

#### REACTIONS IN THE WET WAY.

1. **Caustic Potash** precipitates black mercurous oxide;

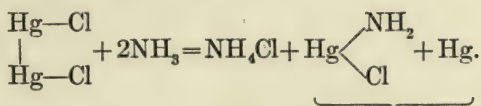


2. **Ammonia** produces a black precipitate of mercuric amino salt with metallic mercury;



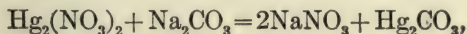
It can easily be shown that this precipitate contains metallic mercury by rubbing a piece of pure gold over it, when silver-lustrous gold amalgam will be formed.

Mercurous chloride gives with ammonia a mercuric amine with separation of metallic mercury:

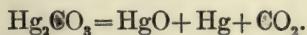


By boiling the black precipitate with dilute hydrochloric acid or with concentrated ammonium chloride solution, the mercuric amine goes into solution, leaving behind drops of mercury.

3. **Alkali Carbonates** give, first, a yellow precipitation of the carbonate, which quickly become gray, owing to the formation of mercuric oxide, metallic mercury, and carbon dioxide:



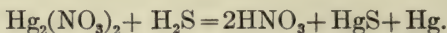
and



4. **Ammonium Carbonate** yields the same precipitate as ammonia.

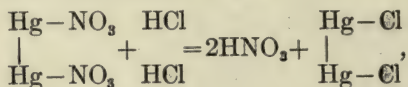


**5. Hydrogen Sulphide** immediately throws down a black precipitate of mercuric sulphide and mercury (difference from mercuric salts):



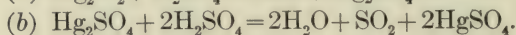
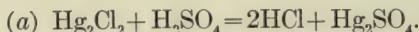
The black precipitate does not dissolve completely in potassium sulphide, the mercury remaining insoluble, but in alkali polysulphides it dissolves.

**6. Hydrochloric Acid and Soluble Chlorides** precipitate white mercurous chloride (calomel),

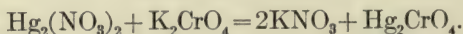


insoluble in water and dilute acids, soluble in strong nitric acid and aqua regia. On boiling for a long time with water, calomel becomes gray, owing to a partial decomposition into mercuric chloride and mercury.

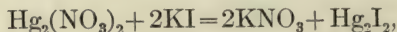
On boiling with concentrated sulphuric acid, mercuric sulphate is formed with evolution of sulphur dioxide and hydrochloric acid:



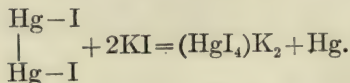
**7. Neutral Potassium Chromate** precipitates red mercurous chromate on boiling (cf. p. 107):



**8. Potassium Iodide** precipitates green mercurous iodide,



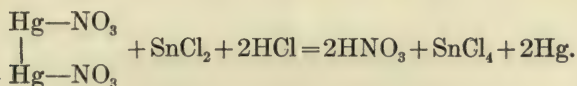
soluble in an excess of the precipitant, with the formation of mercuric potassium iodide and separation of mercury:



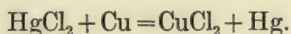
**9. Potassium Cyanide** precipitates metallic mercury, mercuric cyanide being formed at the same time:



## 10. Stannous Chloride precipitates gray metallic mercury:

**Detection of Mercury in Urine.\***

From 500 to 1000 c.c. of urine are treated in a beaker with 0.5 per cent of hydrochloric or sulphuric acid, 0.5 gm. of brass wool (such as is used for the ornamentation of Christmas trees) is added, and, while heating on the water-bath to 60 or 80°, an air stream is conducted through the liquid for from 10 to 15 minutes, to keep it in constant motion. Any mercury present is replaced by copper:



The mercury, as fast as it is set free, amalgamates with the excess of copper present. The liquid is poured off from the tiny threads of brass and the latter are washed thoroughly by decantation with distilled water, then with alcohol, and finally with ether. The brass threads are pressed between layers of filter-paper, to free them from any adhering ether, and rolled between the fingers into a small ball which is introduced into a thoroughly cleansed and perfectly dry glass tube, 10 cm. long, 0.5 cm. wide and closed at one end. With the aid of the blast flame, a capillary of about 1 mm. width is made in the tube about 0.5 cm. away from the brass, toward the open end of the tube. After cooling the tube the bottom of it, in which the sample rests, is heated to dark redness. This causes the mercury to distil off and it is condensed in a gray mirror consisting of tiny drops in the colder portion of the tube. If any considerable amount of mercury is present, *e.g.*, more than 1 mg., the drops of mercury can be distinctly seen with a lens. If less than 1 mg. of mercury is present in the urine, it is very difficult to distinguish the mirror. In this case to make it perceptible, the mercury is transformed into scarlet-red mercuric iodide. For this purpose, a tiny grain

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\*P. Fübringer, Z. anal. Chem. 27, 526 (1888).

of iodine is placed in a test-tube and the tube containing the mercury mirror is cut off just above the place where the ball of brass rests and placed in the test-tube. The lower part of the glass is now cautiously heated over a gas flame. As soon as the violet vapors of iodine reach the place where the mercury was deposited, the latter is transformed, by very gentle heating, into the red iodide, which can be seen most distinctly by removing the little tube and laying it upon a piece of white paper. This method is very sensitive and permits the positive recognition of as little as 0.4 mgm. of  $\text{HgCl}_2$ .\*

### Detection of Mercury Vapors in the Air.

A piece of pure gold leaf is placed in a small glass tube and the air to be tested is aspirated through the tube for an hour, at a rate not greater than one liter per minute. Meanwhile a Geissler tube, of the form shown in Fig. 19, is evacuated by means of a water pump (not a mercury pump!) after which both cocks are closed. The wad of gold leaf, which now contains as amalgam any mercury that was present in the air tested, is placed in the tube *n* and by suddenly opening the cock *a*, which has a wide bore, the gold is sucked into the tube and stops at *c*, the mouth of the capillary opening. The next step is to replace the air in the tube by hydrogen. Hydrogen gas from a Kipp generator, dried by passing it through concentrated sulphuric acid, is introduced at *a* and allowed to pass out at *b*. After a rapid stream of the gas has passed through the tube for three minutes, the cocks *a* and *b* are closed, without disconnecting the Kipp generator, *b* is connected with the suction pump† and the apparatus is evacuated for a minute or two, after which *b* is closed, and *a* opened (which causes more hydrogen to enter the apparatus); then *a* is closed again, *b* opened and the apparatus once more evacuated. This alternate introduction of hydrogen gas and evacuation is repeated five or six times. In this way the air

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\* For other methods of detecting mercury in urine, see Jolles, *Z. anal. Chem.* **39**, 230 (1900), Merget, *J. Pharm. Chim.* [5] **19**, 444 (1889); and Oppenheim, *Z. anal. Chem.* **42**, 431 (1903).

† Between the water suction-pump and the Geissler tube, a calcium chloride drying tube should be introduced.



is entirely replaced by hydrogen. The tube is finally evacuated for five or ten minutes and at the last the cock *b* is closed. The capillary is placed in front of the slit of a spectroscope and the secondary current of an induction apparatus is allowed to pass through the tube. In the presence of the merest trace of mercury, the characteristic green line  $546\ \mu\mu$  is distinctly visible in the cold, and with somewhat larger amounts of mercury the indigo-blue line at  $456\ \mu\mu$  can be seen. If the wad of gold leaf is cautiously warmed with the Bunsen flame, the mercury spectrum appears still more sharply.

*Remark.* This test is so extremely sensitive that a blank test performed in places where work with mercury has been performed will often show the presence of this element in the atmosphere.

If the apparatus has been used for the detection of mercury it must be thoroughly cleansed before it is used again for this purpose. To this end, the gold is removed, and aqua regia after being sucked into the tube is allowed to remain there for several minutes. The acid is run out and the tube is rinsed three times with distilled water, once with absolute alcohol\* and finally dried by passing dry hydrogen through the tube for five minutes, while warming it at the same time. The gold is ignited gently to distil off any mercury it contains. If now on introducing the gold and evacuating the apparatus, the mercury spectrum is no longer visible, the tube is ready for a new experiment.

It may be mentioned that the two platinum wires in the Geissler tube must not be provided with aluminium points because

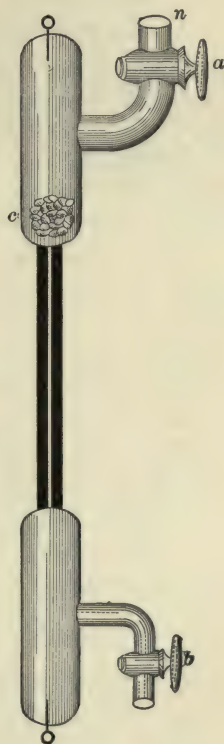


FIG. 19.

\* All these operations must be carried out in a space where there are positively no mercury vapors present in the atmosphere.

aluminium amalgamates with mercury and when the points are once amalgamated it is impossible to free the tube sufficiently from mercury to permit its use for subsequent experiments.

#### REACTIONS OF MERCURY IN THE DRY WAY.

Almost all mercury compounds sublime on being heated in the closed tube.

Mercuric chloride melts first, then vaporizes, forming a crystalline deposit on the cold sides of the tube.

Mercurous chloride sublimes; the sublimate is almost white, but there is a slight grayish tint owing to the decomposition of a small part of the substance into mercuric chloride and mercury.

Mercuric iodide yields a yellow sublimate, which becomes red on being rubbed with a glass rod.

Mercury compounds containing oxygen (all more or less unstable) yield mercury.

The sulphide gives a black sublimate.

All compounds of mercury, when mixed with sodium carbonate and heated in a closed tube, yield a gray mirror, consisting of small globules of mercury. In order to make the drops more apparent a piece of filter-paper is placed over a glass rod, with which the mirror is rubbed. The small drops then run together into large ones, stick to the paper, and can be removed from the glass.

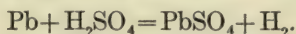
#### LEAD, Pb. At. Wt. 207.1.

[Sp. Gr. = 11.36–11.39. M. Pt. = 327.4° C. B. Pt. = 1600° C.]

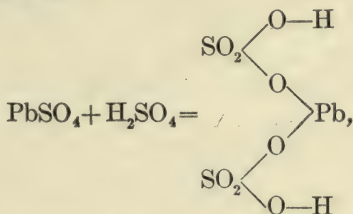
*Occurrence.*—Galena,  $\text{PbS}$ , isometric; cerussite,  $\text{PbCO}_3$ , orthorhombic and isomorphous with aragonite,  $\text{CaCO}_3$ , anglesite,  $\text{PbSO}_4$ , orthorhombic, isomorphous with anhydrite,  $\text{CaSO}_4$ , celestite,  $\text{SrSO}_4$ , and barite,  $\text{BaSO}_4$ ; pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , hexagonal; mimetite,  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ; vanadinite,  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ . The last three minerals are isomorphous and belong to the apatite group. Other minerals which may be mentioned are wulfenite,  $\text{PbMoO}_4$ , tetragonal, isomorphous with stolzite,  $\text{PbWO}_4$ , and the monoclinic crocoite,  $\text{PbCrO}_4$ .

Lead is a bluish-gray metal. It is attacked by all acids. As, however, most lead salts are difficultly soluble in water, it usually becomes coated with a layer of salt, which protects it

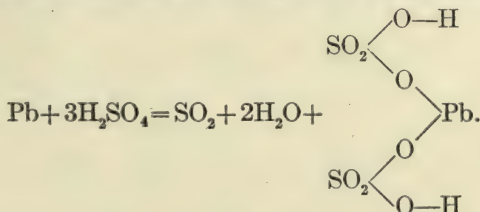
from further action of the acid. Thus lead is immediately attacked by dilute sulphuric acid according to the equation



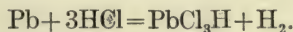
But, as the lead sulphate formed is insoluble in dilute sulphuric acid, the reaction quickly ceases. Upon this principle rests the use of "lead chambers" in the manufacture of sulphuric acid, and the use of "lead pans" for the concentration of the dilute "chamber acid." It has, however, been found from experience that the sulphuric acid should not be concentrated too much in lead pans—stopping when a 78–82 per cent. acid is obtained. The protecting layer of lead sulphate is soluble in hot concentrated sulphuric acid, forming soluble lead bisulphate,



so that the hot concentrated acid can act on the lead anew:



Lead behaves quite similarly on treatment with hydrochloric acid. On the surface a protecting coating of lead chloride is obtained, which is soluble in hot concentrated hydrochloric acid, forming  $\text{PbCl}_3\text{H}$ . Lead is therefore soluble in concentrated hydrochloric acid:

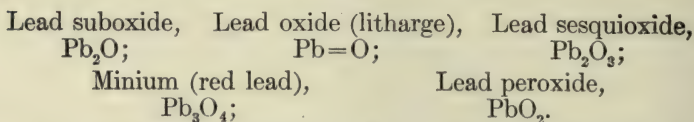


Hydrofluoric acid attacks lead similarly, forming a protecting layer of lead fluoride, which is insoluble in hydrofluoric acid. Consequently lead retorts can be used for the distillation of hydrofluoric acid and in the preparation of hydrofluoric acid by means of fluorite and sulphuric acid.



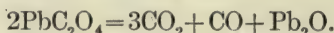
Nitric acid is the proper solvent for lead. Lead nitrate is insoluble in strong nitric acid, so that lead does not dissolve in concentrated nitric acid; the solution must be sufficiently dilute to prevent the separation of the lead nitrate formed.

Lead forms the following oxides:



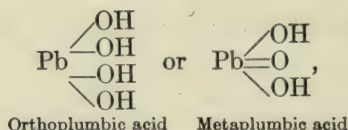
Of these oxides,  $\text{PbO}$  alone is the anhydride of a base;\* from it the salts of lead are derived, in which the lead is bivalent. This lead monoxide (litharge) is a yellow powder, which melts at about  $980^\circ \text{C}$ ., and solidifies on slow cooling, forming tetragonal crystals (needles). It is slightly soluble in water with an alkaline reaction, and is readily soluble in dilute nitric acid.

Lead suboxide,  $\text{Pb}_2\text{O}$ , is formed as a black velvety powder on heating the oxalate to about  $300^\circ \text{C}$ ..



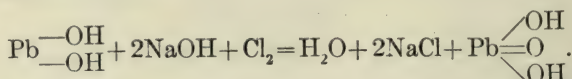
On heating the suboxide in the air, it becomes readily oxidized to lead monoxide.

Lead dioxide,  $\text{PbO}_2$ , must be considered as the anhydride of the acids:



just as  $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{CO}_2$ ,  $\text{MnO}_2$ , are anhydrides of silicic, stannic, carbonic, and manganous acids. The acid  $\begin{array}{c} \text{OH} \\ \diagup \\ \text{Pb} = \text{O} \\ \diagdown \\ \text{OH} \end{array}$  is formed by

the oxidation of lead hydroxide,  $\text{Pb}(\text{OH})_2$ , in alkaline solution by means of hypochlorites, chlorine, bromine, hydrogen peroxide, or potassium persulphate:




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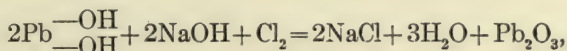
\* Although  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$  is known.

The brown metaplumbic acid which separates out goes over at 100° C. into the anhydride; and the latter on ignition loses oxygen, changing into yellow lead monoxide. The other two oxides of lead,  $\text{Pb}_2\text{O}_3$  and  $\text{Pb}_3\text{O}_4$ , must be regarded as salts of the plumbic acids;

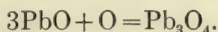
$\text{Pb}_2\text{O}_3$  as the salt of metaplumbic acid:  $\text{Pb} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{=O} \\ \diagdown \text{O} \diagup \end{array} \text{Pb}$ ; and  $\text{Pb}_3\text{O}_4$  as

the salt of the hypothetical orthoplumbic acid:  $\text{Pb} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{=O} \\ \diagdown \text{O} \diagup \end{array} \text{Pb} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{=O} \\ \diagdown \text{O} \diagup \end{array} \text{Pb}$ .

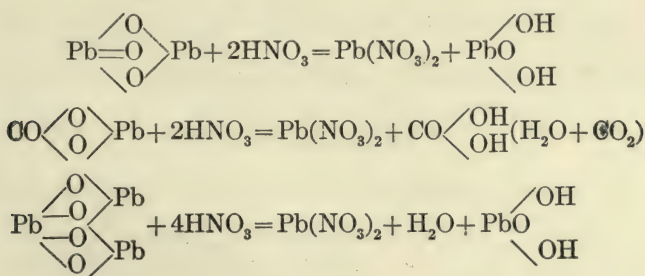
$\text{Pb}_2\text{O}_3$  is obtained as a yellow precipitate on gently oxidizing an alkaline solution of lead monoxide by means of hypochlorites, halogens, hydrogen peroxide, or persulphates:



and the red minium,  $\text{Pb}_3\text{O}_4$ , by igniting lead oxide or lead carbonate for some time in the air at about 430° C.:



Both  $\text{Pb}_2\text{O}_3$  and  $\text{Pb}_3\text{O}_4$  behave chemically as salts; for, on treating with nitric acid, brown plumbic acid and lead nitrate are formed, which corresponds to the action of nitric acid on, say, lead carbonate:

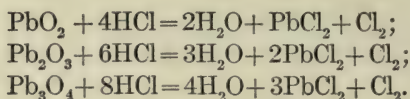


These salt-like oxides\* are perfectly analogous to those of manganese; on treatment with hydrochloric acid they yield chlo-

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\* Besides the lead salts of plumbic acid, alkali and alkaline earth salts are known.

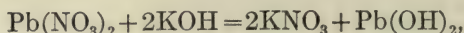
rine, the plumbic acid, at first set free, behaving like a peroxide:



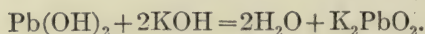
#### REACTIONS IN THE WET WAY.

Lead salts are difficultly soluble or insoluble in water; but all dissolve in dilute nitric acid, excepting, perhaps, fused lead chromate, which is very difficultly soluble.

1. **Potassium and Sodium Hydroxides** precipitate white lead hydroxide:



soluble in an excess of the precipitant, forming a plumbite.\*

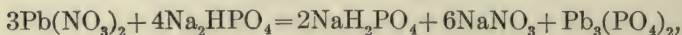


$\text{Pb}(\text{OH})_2$  is also slightly soluble in water, except when it contains carbonic acid. The aqueous solution of lead hydroxide is slightly alkaline.

2. **Ammonia** precipitates the white hydroxide, insoluble in excess of the reagent.

3. **Alkali Carbonates** precipitate white basic lead carbonate. *Alkali bicarbonates* precipitate the normal carbonate.

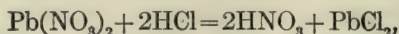
4. **Sodium Phosphate** precipitates white lead phosphate:



insoluble in acetic acid, readily soluble in nitric acid, caustic soda or potash.

5. **Potassium Cyanide** precipitates white lead cyanide, insoluble in an excess.

6. **Hydrochloric Acid or Soluble Chlorides** precipitate from moderately concentrated solutions flocculent, white lead chloride:



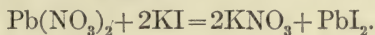

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\* According to Hantzsch, *Z. anorg. Chem.*, **30**, (1902), p. 289, the alkaline solution contains the lead as  $\text{Pb} \begin{array}{c} \diagup \text{H} \\ \text{O} \\ \diagdown \text{OK} \end{array}$ .



difficultly soluble in cold water (135 parts of water dissolve 1 part of  $\text{PbCl}_2$ ), but much more soluble in hot water; on cooling the solution, lead chloride separates in the form of glistening needles or plates. Lead chloride is much more soluble in concentrated hydrochloric acid and in a concentrated solution of a chloride of an alkali than it is in water, as it forms complex compounds with these substances, which are, however, decomposed on dilution with water, with separation of lead chloride.

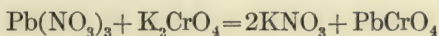
7. **Potassium Iodide** precipitates yellow lead iodide:



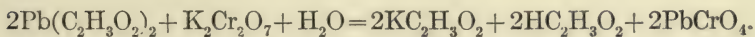
The iodide is much more insoluble in water than the chloride (194 parts of boiling water dissolve only 1 part of lead iodide), forming a colorless solution from which lead iodide separates on cooling, in the form of gold-yellow plates.

The iodide dissolves to a considerable extent in hydriodic acid, and in a solution of an alkali iodide, forming lead hydriodic acid;  $\text{PbI}_3\text{H}$  or one of its salts (such as  $\text{PbI}_3\text{K}$ ), all of which are decomposed on dilution, with deposition of lead iodide.

8. **Alkali Chromates** produce a yellow precipitate of lead chromate:

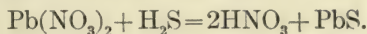


and

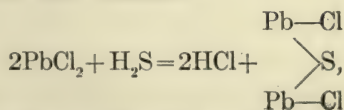


Lead chromate is insoluble in acetic acid, but soluble in nitric acid and in caustic alkali.

9. **Hydrogen Sulphide** produces in the most dilute lead solutions (from slightly acid solutions, as well as from neutral or alkaline ones) a black precipitate of lead sulphide:



From hydrochloric acid solutions an orange-red precipitate of lead sulphochloride is at first obtained:



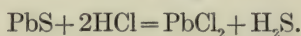
which is decomposed immediately by more hydrogen sulphide, forming the black lead sulphide. In this respect lead salts are similar to mercuric salts (see page 174).

Lead sulphide is soluble in dilute, boiling, double-normal nitric acid, forming lead nitrate, with separation of sulphur:

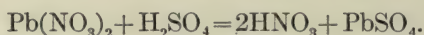


The reaction usually goes a little further; some of the sulphur is oxidized to sulphuric acid, forming insoluble lead sulphate. The amount of sulphuric acid formed (and therefore of the lead sulphate also) increases with the concentration of the acid.

Lead sulphide is also soluble in strong hydrochloric acid.



**10. Sulphuric Acid and Soluble Sulphates** cause in solutions of lead salts the separation of white difficultly-soluble lead sulphate:



One part of the salt dissolves at the ordinary temperature in 22,800 parts of water; in water containing a little sulphuric acid it is still less soluble, while in alcohol it is insoluble. Lead sulphate dissolves perceptibly in nitric acid; in hot concentrated hydrochloric acid it is completely soluble. On cooling the hydrochloric acid solution, lead chloride separates out in needles.

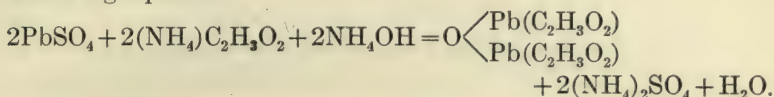
Lead sulphate is also soluble in concentrated sulphuric acid,\* readily on boiling and considerably in the cold, forming acid lead sulphate which is decomposed by water into sulphuric acid and lead sulphate. Almost all the sulphuric acid of commerce contains some dissolved lead sulphate. In order to detect this, 200–300 c.c. of the concentrated acid should be diluted with an equal volume of water and allowed to stand twelve hours, whereby the lead sulphate separates as a white powder.

Besides being soluble in acids, lead sulphate is easily soluble in caustic alkalies, and in solutions containing the ammonium salts of many organic acids. This last property is of great importance for the analytical chemist, as it offers a means for separating lead sulphate from barium sulphate, silica, etc., which remain undissolved. Ammonium acetate or ammonium tartrate is usually used as the solvent.

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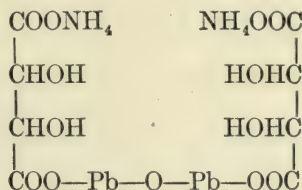
\* Cf. page 183.

The solution of lead sulphate by means of a *concentrated* solution of ammonium acetate takes place probably according to the following equation:



From this solution the lead can be precipitated as chromate by the addition of potassium chromate or as sulphate upon the addition of dilute sulphuric acid.

According to Kahlenberg and Schreiner\* lead sulphate dissolves in ammonium tartrate in the presence of ammonia with the formation of



#### REACTIONS IN THE DRY WAY.

Heated with sodium carbonate on charcoal, all lead compounds yield a malleable button, surrounded with an incrustation of the yellow oxide. On the charcoal stick also, the malleable button is readily obtained.

Lead glasses turn black on heating in the reducing flame, owing to the separation of lead.

#### BISMUTH, Bi. At. Wt. 208.0.

Sp. Gr. = 9.8. M. Pt. = 268° C. B. Pt. about 1435° C.

*Occurrence.*—Bismuth usually occurs native with nickel and cobalt ores. The following ores are of no great importance: Bismite,  $\text{Bi}_2\text{O}_3$ ; bismuthinite,  $\text{Bi}_2\text{S}_3$ ; emplectite,  $\text{Bi}_2\text{S}_4\text{Cu}_2$ ; bismutite,  $3[\text{CO}_3][\text{BiOH}] \cdot 5\text{Bi}(\text{OH})_3$ .

Bismuth is a brittle, reddish-white metal which crystallizes in the hexagonal system. The proper solvent for bismuth (as is the case with most other metals) is nitric acid. Hydrochloric acid does not attack bismuth, and sulphuric acid dissolves it only on warming.

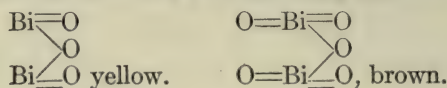
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\* Z. phys. Chem. 17, 590.



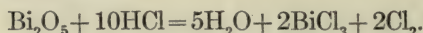
Bismuth forms two oxides:

Bismuth trioxide and bismuth pentoxide.

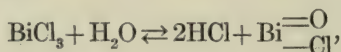


Bismuth is either trivalent or quinquivalent like nitrogen, phosphorus, arsenic, and antimony.

Bismuth trioxide is a basic anhydride,\* from which the salts are derived. Bismuth pentoxide, a brownish substance, acts as an acid anhydride, forming an acid  $\text{HBiO}_3$ ,\* corresponding to metaphosphoric acid. Salts of this acid have never been prepared in a pure state. On igniting,  $\text{Bi}_2\text{O}_5$  loses oxygen, forming yellow  $\text{Bi}_2\text{O}_3$ . It dissolves in hydrochloric acid with evolution of chlorine, forming a salt of trivalent bismuth:

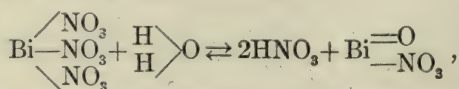


Bismuth salts are mostly colorless, and are all insoluble in considerable water, on account of being hydrolyzed into an insoluble basic salt; thus the chloride is quantitatively decomposed into bismuth oxychloride:



insoluble in tartaric acid (difference from antimony).

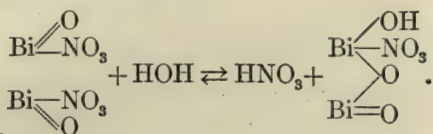
Bismuth oxychloride is readily soluble in hydrochloric acid, the above equation taking place from right to left. The reaction therefore is reversible and the relative amounts of water and hydrochloric acid present determine in which direction the reaction will go. On adding water to a slightly acid solution of  $\text{BiCl}_3$ , a white precipitate of the oxychloride appears immediately. On carefully adding hydrochloric acid, the precipitate again dissolves, but may be reprecipitated by the addition of more water. All the other compounds of bismuth act as the chloride. The nitrate yields, at first, an amorphous precipitate of  $\text{BiONO}_3$ :




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\* Bismuth trioxide acts as a weak acid under some circumstances (cf. foot-note p. 191).

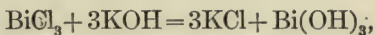
which becomes more basic on further addition of water, becoming crystalline at the same time:



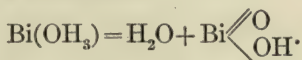
This last compound is the *bismuth subnitrate* which is so much used in medicine.

#### REACTIONS IN THE WET WAY.

1. **Potassium Hydroxide** precipitates, in the cold, white bismuth hydroxide:

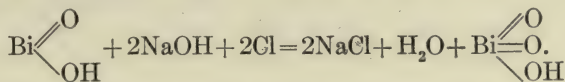


which, on boiling, becomes faint yellow, because it loses water and forms a less hydrated hydroxide:



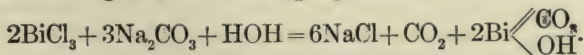
Both of these hydroxides are insoluble in an excess of the precipitant,\* but are readily soluble in acids.

On adding to the alkaline solution, in which the hydroxide is suspended, chlorine, bromine, hypochlorites, or hydrogen peroxide, the white or yellowish precipitate becomes brown, owing to the formation of bismuthic acid:



2. **Ammonia** precipitates a white basic salt (not the hydroxide), the composition of which varies with the concentration and with the temperature.

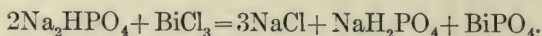
3. **Alkali Carbonates** precipitate, according to the temperature and concentration, a number of basic carbonates; one of which is formed according to the following equation:



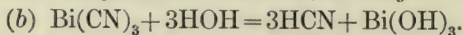
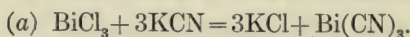

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\* In very concentrated KOH,  $\text{Bi}(\text{OH})_3$  dissolves on warming. On cooling, part of the  $\text{Bi}(\text{OH})_3$  is precipitated, and on dilution all of it. In this case the hydroxide acts as a weak acid, like antimony trioxide.

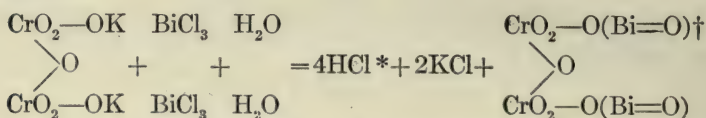
4. **Sodium Phosphate** precipitates the white, granular phosphate, insoluble in dilute nitric acid, difficultly soluble in hydrochloric:



5. **Potassium Cyanide** precipitates the white hydroxide (not the cyanide). The cyanide is at first formed, but is hydrolyzed:

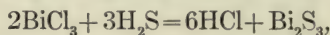


6. **Potassium Dichromate** precipitates yellow bismuthyl dichromate:



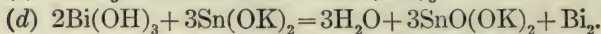
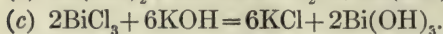
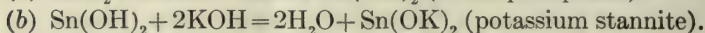
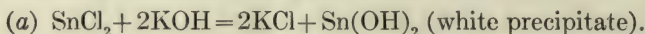
soluble in mineral acids, insoluble in caustic alkalis (difference from lead).

7. **Hydrogen Sulphide** precipitates brown bismuth sulphide:



insoluble in cold dilute mineral acids and alkaline sulphides, soluble in hot dilute nitric acid, and in boiling, concentrated hydrochloric acid.

8. **Alkali Stannites** (an alkaline solution of stannous chloride) cause a black precipitation of metallic bismuth.† This very sensitive reaction is performed as follows: To a few drops of stannous chloride, caustic alkali is added until the white precipitate at first produced dissolves clear, and the bismuth solution is then added in the cold; on shaking, a black precipitate immediately appears. The following reactions take place in this test:



Potassium stannate.

---

\* An excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  should be employed to prevent the solvent action of the hydrochloric acid; the hydrochloric acid is then used up as follows:



† The univalent group (BiO) is called bismuthyl.

‡ Vanino & Treubert, Ber. 1898, 1113.

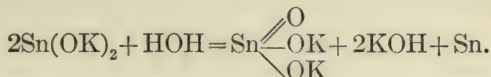


So that the whole reaction may be represented as follows:

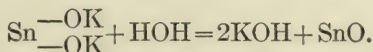


In making this test, a too concentrated caustic alkali solution should be avoided; and the solution must be kept cold, otherwise the stannite itself may give a black precipitate.

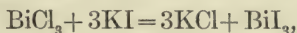
1. If too much caustic potash is used, metallic tin will separate out:



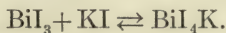
2. If too little caustic potash is used, black stannous oxide will be thrown down in the cold, after long standing; quickly on boiling:



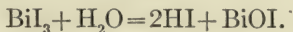
9. Potassium Iodide precipitates black bismuth iodide:



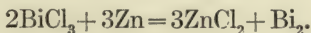
soluble in excess of the reagent, with a yellow to orange color:



By diluting this last solution with not too much water, the black iodide is reprecipitated, which, on the addition of more water, is changed into orange-colored basic iodide:



10. Metallic Zinc precipitates metallic bismuth:

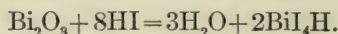


#### REACTIONS IN THE DRY WAY.

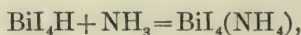
Bismuth salts color the non-luminous flame a pale greenish white. Heated with soda on charcoal before the blowpipe, a brittle button of the metal is obtained, surrounded by a yellow incrustation of bismuth oxide.

On heating a compound of bismuth in the upper reducing flame (page 37) of the Bunsen burner, the bismuth is reduced to metal,

which is volatilized and burnt to oxide in the upper oxidizing flame. On holding a porcelain evaporating-dish (glazed on the outside and filled with water) just above the oxidizing flame, a barely visible deposit is obtained, which, on being treated with hydriodic acid,\* is changed to scarlet bismuth hydriodic acid:



By breathing on this deposit, the color disappears, but reappears as soon as the moisture has evaporated. On exposure to fumes of ammonia (by blowing the vapors away from the stopper of an ammonia bottle) the deposit is colored a beautiful orange, owing to the formation of the ammonium salt of the bismuth hydriodic acid:



which also becomes invisible on being breathed upon.

By moistening this coating with an alkaline solution of stannous chloride, black metallic bismuth is deposited.

**COPPER, Cu. At. Wt. 63.57.**

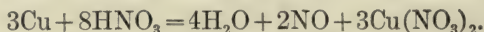
Sp. Gr. = 9.84. M. Pt. = 1080° C.

*Occurrence.*

Native copper, Cu Isometric	Cuprite, Cu <sub>2</sub> O Isometric	Chalcocite, Cu <sub>2</sub> S Orthorhombic	Chalcopyrite, CuFeS <sub>2</sub> Tetragonal
Malachite, Cu—OH \ CO <sub>3</sub> Cu—OH Monoclinic, often pseudomorphous after cuprite	Azurite, Cu—OH \ CO <sub>3</sub> Cu \ CO <sub>3</sub> Cu—OH Monoclinic	Atacamite. Cu—Cl \ O + H <sub>2</sub> O. Cu—OH Orthorhombic	

Copper is a light red, ductile metal.

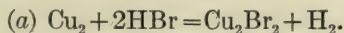
The proper solvent for copper is nitric acid:




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\* The hydriodic acid is easiest obtained by moistening a piece of asbestos, held in the loop of a platinum wire, in a solution of alcoholic iodine solution and then setting fire to the moist asbestos. By holding the burning asbestos under the dish, enough hydriodic acid is formed to change the bismuth oxide into the red compound.

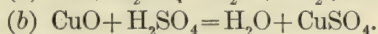
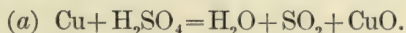
Bright copper is not dissolved by hydrochloric acid alone, but in the presence of a weak oxidizing agent, e.g., ferric chloride, the solution of the metal is easily effected. Hot hydrobromic acid dissolves it with evolution of hydrogen, forming cuprous hydrobromic acid:



At the beginning of this reaction the solution usually turns dark violet on account of the formation of the cupric salt of cuprous hydrobromic acid, owing to the copper being somewhat oxidized on the surface. In this case, however, the solution soon becomes colorless; the cupric salt is reduced by the nascent hydrogen. On adding water to the clear solution cuprous bromide is precipitated.

Copper is not attacked by dilute sulphuric acid, but it dissolves in hot concentrated sulphuric acid, forming cupric sulphate with evolution of sulphur dioxide.

The copper is at first oxidized (at the cost of the sulphuric acid) to cupric oxide, and this latter dissolves in more of the acid:



Copper forms two oxides: red cuprous oxide,  $\text{Cu}_2\text{O}$ , and black cupric oxide,  $\text{CuO}$ .

Both oxides are basic anhydrides, forming cuprous and cupric salts. Salts of the cuprous series contain the bivalent cuprous

group,\*  $\begin{array}{c} \text{Cu}— \\ | \\ \text{Cu}— \end{array}$ , while those of the cupric series contain the simple,

bivalent copper atom  $\text{Cu} < .^\dagger$

\* E. Beckmann, *Z. anorg. Chem.* **55**, 179 (1907).

† Copper is also known in the trivalent condition. If a nitric acid solution of tellurous acid is evaporated to dryness with a little copper nitrate and the residue is treated with KOH solution (1:5) it dissolves. If to the clear solution 4 to 6 gm. of  $(\text{NH}_4)_2(\text{SO}_4)_2$  are added, little by little, while the solution is at the temperature of the water bath, it becomes pink and the tellurium is present for the most part as telluric acid but to some extent as the potassium salt of telluro-cupric acid:  $\text{K} \left[ -\text{O}-\text{Cu}''' \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{TeO}_2 \right]$ . Cf. Moser: *Z. anorg. Chem.* **54**, 119 (1907) and Brauner and Kuzma, *Ber.*, **1907**, 3362.

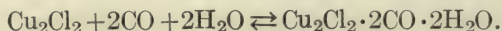


### A. Cuprous Compounds.

The cuprous compounds are extremely unstable, being oxidized quickly to cupric compounds. The only known cuprous salts are those with the halogens;\* these are colorless, insoluble in water, but readily soluble in concentrated halogen acids, forming colorless solutions. Such solutions contain the unstable cuprous halogen acids, probably of the formula  $[\text{Cu}_2\text{X}_6]\text{H}_4$ , in which "X" is either chlorine, bromine, or iodine. Salts are known which are derived from these acids, *e.g.*,  $[\text{Cu}_2\text{Cl}_6]\text{K}_4$ .

The cuprous halogen acids are changed dark on contact with air—the chloride, brownish black; the bromide, dark violet; probably due to the formation of cupric salts of the cuprous halogen acids.

The behavior of the cuprous halogen acids toward carbon monoxide is very important; the latter is readily absorbed, forming an unstable compound:

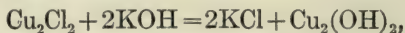


By boiling the solution the compound is decomposed into cuprous chloride and carbon monoxide; cuprous chloride is used in gas analysis for the absorption of this gas.

#### REACTIONS IN THE WET WAY.

A solution of cuprous chloride in hydrochloric acid should be used, which may be prepared as follows: Two gms. of cupric oxide are dissolved in 25 cc. of hydrochloric acid (Sp. Gr. 1.12); the solution is poured into a flask and 0.58 gram of copper filings is added; a copper spiral is placed in the flask, one end of which reaches into its neck; the flask is then stoppered and allowed to stand a few days. The originally dark solution will gradually become colorless, when it is ready to be used for the following reactions:

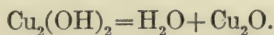
1. **Potassium Hydroxide** produces in the cold a yellow precipitate of cuprous hydroxide:



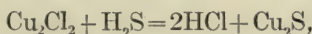

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\*  $\text{Cu}_2\text{SO}_4$  is said to exist in solution.

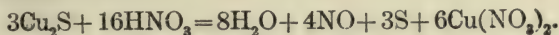
which loses water at the boiling temperature, changing to red cuprous oxide:



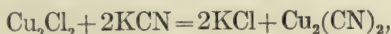
2. **Hydrogen Sulphide** precipitates black cuprous sulphide:



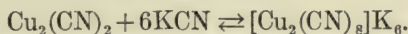
soluble in warm dilute nitric acid, forming blue cupric nitrate, with separation of sulphur:



3. **Potassium Cyanide** precipitates white cuprous cyanide:



soluble in excess, forming colorless potassium cuprocyanide:



This solution contains no cuprous ions, but ions of cuprocyanide,  $[\text{Cu}_2(\text{CN})_8]$ , and potassium, and gives no precipitation with potassium hydroxide or hydrogen sulphide. This property is made use of in the separation of copper from cadmium.

Potassium cuprocyanide, on being diluted with considerable water, forms successively the following compounds:  $[\text{Cu}_2(\text{CN})_4]\text{K}_2$ ,  $[\text{Cu}_2(\text{CN})_3\text{H}_2\text{O}]\text{K}$ , and finally  $\text{Cu}_2(\text{CN})_2$ . All of these compounds, even in the solid state, are decomposed by hydrogen sulphide with precipitation of black cuprous sulphide. Consequently, *in order to prevent the precipitation of copper by hydrogen sulphide, considerable potassium cyanide must be added, more than enough to form the salt  $[\text{Cu}_2(\text{CN})_8]\text{K}_6$ .*

## B. Cupric Compounds.

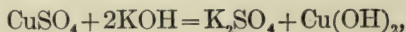
Cupric salts are either blue or green in aqueous solution; in the anhydrous state they are white or yellow.

The chloride, nitrate, sulphate and acetate are soluble in water; most of the remaining salts are insoluble in water, but readily soluble in acids.

## REACTIONS IN THE WET WAY.

A solution of copper sulphate should be used.

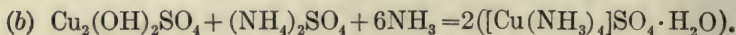
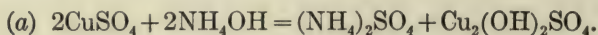
1. **Potassium Hydroxide** produces in the cold a blue precipitate of cupric hydroxide:\*



which on boiling becomes changed into brownish-black cupric oxide.

In the presence of tartaric acid, citric acid, and many other organic hydroxy-compounds, cupric hydroxide is not precipitated by the addition of caustic alkali, but the solution is colored an intense blue. If this alkaline solution is treated with *d*-glucose, aldehydes, arsenious acid or various other substances having a reducing power, yellow cuprous hydroxide is precipitated from the warm solution which is changed to red cuprous hydroxide on boiling. An alkaline solution of cupric salt containing tartaric acid is commonly used under the name of Fehling's solution. It may be prepared by mixing together equal volumes of a solution containing 34.639 gms. of crystallized copper sulphate in 500 c.c. of water and with a solution consisting of 173 gms. Rochelle salt and 52 gms. NaOH in 500 c.c. of water. It is best to keep the solutions separate until they are to be used. Fehling's solution is a reagent for many kinds of sugar, aldehydes, hydroxylamine, etc.

2. **Ammonia**.—On adding ammonia cautiously to the solution of a cupric salt, a green powdery precipitate of a basic salt is obtained, which is extremely soluble in an excess of the reagent, forming an azure-blue solution:



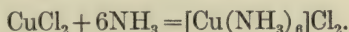
On adding alcohol to the concentrated blue solution, the above compound is precipitated as a blue-violet crystalline substance,

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\*  $\text{Cu}(\text{OH})_2$  dissolves in very concentrated KOH or NaOH, particularly on warming, with a blue color. Cf. page 156, Remark.

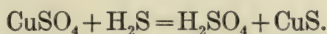


which gradually loses ammonia on being heated, leaving behind the cupric salt. On conducting ammonia gas over an anhydrous copper salt, the ammonia is eagerly absorbed, with the formation of a complex cupric ammonia salt:



These compounds (which contain as a maximum  $6\text{NH}_3$  to one atom of copper) are perfectly analogous to the corresponding compounds of nickel, cobalt, and zinc. By the precipitation of the ammoniacal solution with alcohol, the compound with  $4\text{NH}_3$  to one atom of copper is always obtained.

(3) **Hydrogen Sulphide** precipitates from neutral or very slightly acid solutions colloidal, black cupric sulphide; which, as part of it is usually in the form of hydrosol, has a tendency to run through the filter.

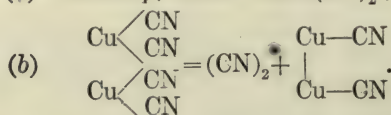
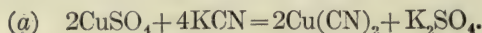


To prevent the formation of hydrosol, the solution must contain some electrolyte; the hydrochloric acid present when the precipitation is made is usually sufficient. Another difficulty frequently encountered is due to the readiness with which a part of the cupric sulphide precipitate is oxidized to sulphate by contact with the air. Thus if a filter containing copper sulphide is allowed to stand in the air, a little cupric sulphate is formed which is soluble in water. Many cases where the cupric sulphide apparently runs through the filter are explained in this way. In filtering a copper sulphide precipitate the rule should be never to let the filter drain completely until the filtration and washing is over and the washing should be with dilute hydrogen sulphide water, which serves to prevent any oxidation.

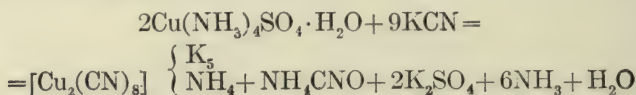
Copper sulphide is soluble in hot dilute nitric acid, but insoluble in boiling dilute sulphuric acid (difference from cadmium); soluble in potassium cyanide, forming potassium cuprous cyanide. From a solution of the latter salt the copper cannot be precipitated by hydrogen sulphide.

Copper sulphide is appreciably soluble in ammonium sulphide, but is insoluble in potassium or sodium sulphide\* (difference from mercury).

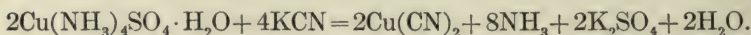
4. **Potassium Cyanide** produces, at first, yellow cupric cyanide, which immediately loses dicyanogen, forming white cuprous cyanide. The latter, as we have already seen, forms soluble potassium cuprous cyanide with more potassium cyanide:



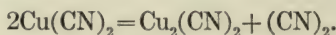
On adding sufficient potassium cyanide to the blue ammoniacal cupric solution, the complex compound will be decolorized, forming cuprous potassium cyanide:



This apparently complicated reaction is in reality quite simple, when we look at the separate steps. First, ammonia is split off, forming the cupric cyanide:



The cupric cyanide then decomposes, as just stated, into cuprous cyanide and dicyanogen:



The cuprous cyanide then dissolves in an excess of the potassium cyanide, forming cuprous potassium cyanide (equation (c) above); and the dicyanogen acts upon the ammonia, forming

\* In solutions of alkali polysulphides, particularly out of contact with the air, cupric sulphide dissolves with the formation of compounds of the type  $\text{NH}_4[\text{CuS}_4]$  and  $\text{K}[\text{CuS}_4]$ . Cf. Hofmann and Höchtlen, *Berichte* **36**, 3090 (1903) and Biltz and Herma, *ibid.* **40**, 974 (1907).

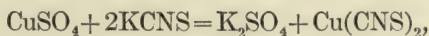
† F. P. Treadwell and G. v. Girssewald, *Z. anorg. Chem.* **38**, 98 (1904). According to Kunschert the symbol of the salt is  $[\text{Cu}(\text{CN})_3]\text{K}_3$ , *Z. anorg. Chem.* **41**, 1260 (1904). See also Grossmann and v. d. Forst, *Z. anorg. Chem.* **43**, 94 (1904).

ammonium cyanide and ammonium cyanate (just as chlorine acts upon caustic potash, forming potassium chloride and potassium hypochlorite):

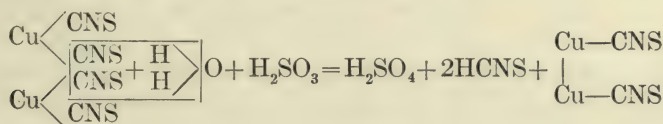


Hydrogen sulphide will not precipitate cupric sulphide from the colorless solution of potassium cupro-cyanide provided sufficient potassium cyanide is present (difference from cadmium). Sometimes, when considerable copper salt is present, the introduction of  $\text{H}_2\text{S}$  causes the formation of a red crystalline precipitate of hydrosulphuric acid,  $(\text{CSNH}_2)_2$ . Cf. page 308.

5. **Potassium Sulphocyanate**,  $\text{KCNS}$ , produces black cupric sulphocyanate:

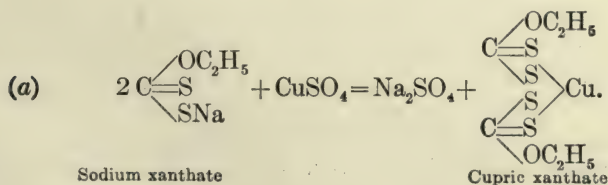


which is gradually changed into white cuprous sulphocyanate, or immediately on adding sulphurous acid:

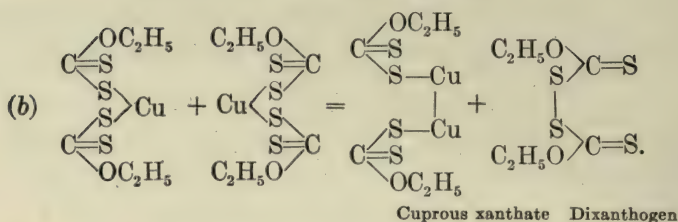


Cuprous sulphocyanate is insoluble in water, dilute hydrochloric acid, and sulphuric acid.

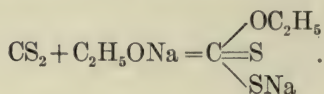
6. **Alkali Xanthates** produce in solutions of cupric salts, at first, a brownish-black precipitate of cupric xanthate, which splits off dioxanthogen, forming finally yellow cuprous xanthate:





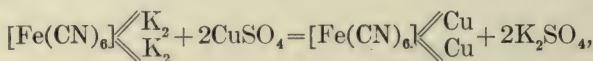


The reagent, sodium xanthate, is readily obtained by mixing carbon disulphide with alcoholic sodium hydroxide:



The alkali xanthates are not used as reagents in testing for copper, but cupric salts are used in testing for xanthates. The reaction is made use of in the detection of carbon disulphide in gas mixtures; the gases are allowed to act upon alcoholic sodium hydroxide, whereby sodium xanthate is formed if carbon disulphide is present, and the solution after neutralizing with acetic acid is tested for xanthate by means of a solution of cupric salt.

7. **Potassium Ferrocyanide** produces in neutral and acid solutions an amorphous precipitate of reddish-brown cupric ferrocyanide:



insoluble in dilute acids, but soluble in ammonia with a blue color. It is also decomposed by potassium hydroxide; in the cold, light-blue cupric oxide and potassium ferrocyanide are formed, while, on warming, black cupric oxide is obtained (difference from uranium, which yields the yellow uranate both with ammonia and sodium or potassium hydroxide).

#### REACTIONS IN THE DRY WAY.

The borax, or salt of phosphorus, bead is green in the oxidizing flame when strongly saturated with the copper salt; blue if containing only a small amount. The reducing flame decolorizes the

bead unless too much copper is present; in such a case it is reddish brown and opaque, owing to the separation of copper. Traces of copper may be determined with certainty as follows: To the slightly bluish bead produced by the oxidizing flame, a trace of tin or of a tin compound is added; the bead is heated in the oxidizing flame until the tin has completely dissolved, when it is slowly brought into the reducing flame and then quickly removed. The bead now appears colorless when hot, but ruby-red and transparent when cold. If, however, the bead is kept too long in the reducing flame, it remains colorless; but the ruby-red color may be produced by cautious oxidation. This reaction is very sensitive, and can also be used for the detection of tin.

Heated with charcoal before the blowpipe (or better still with the charcoal stick), spongy metal is obtained.

Copper salts color the flame blue or green.

CADMIUM, Cd. At. Wt. 112.4.

Sp. Gr. = 8.6. M. Pt. = 320° C. B. Pt. = 770° C.

*Occurrence.*—Cadmium is usually associated with zinc in its ores. It is also found as greenockite, CdS, hexagonal; and as the oxide CdO,\* isometric.

The most important commercial salt is the sulphate,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ . It is not easily recrystallized. To purify the salt, the concentrated aqueous solution is treated with alcohol, and the crystals that are deposited thereby are filtered, washed with alcohol and dried upon blotting paper.

Cadmium is a silver-white, ductile metal. Heated in the air, it burns to brown cadmium oxide. The proper solvent for cadmium is nitric acid. Dilute hydrochloric and sulphuric acids dissolve it but slowly, with evolution of hydrogen. Cadmium forms two oxides:

Cadmium suboxide,  $\text{Cd}_2\text{O}$ , and Cadmium oxide, CdO.

Black

Brown to black.

Cadmium suboxide (whose existence is doubted) is formed with cadmium oxide in small amounts when the metal is burned in the

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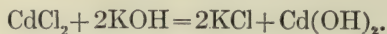
\* With smithsonite in the zinc deposits of Monte Poni, Sardinia. Chem. Ztg. 1901, 561.

air. It is also said to be formed, similar to lead suboxide, by gently heating cadmium oxalate away from air. There are no cadmium salts derived from this oxide. Cadmium forms only one series of salts, in which cadmium is bivalent.

Cadmium salts are mostly colorless, though the sulphide is yellow to orange. Most of the salts are insoluble in water, but readily soluble in mineral acids. The chloride, nitrate, and sulphate are soluble in water.

#### REACTIONS IN THE WET WAY.

1. **Potassium Hydroxide** precipitates white, amorphous cadmium hydroxide, insoluble in an excess of the reagent (difference from zinc and lead):

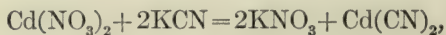


On gently igniting the hydroxide the brown oxide is obtained, which becomes darker on stronger ignition. The ignition of cadmium nitrate yields the black crystalline oxide.

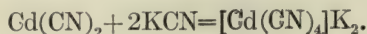
2. **Ammonia** also precipitates the white hydroxide, soluble in excess (difference from lead), forming complex cadmium ammonium compounds, as with zinc, nickel, etc. On diluting with water and boiling, cadmium hydroxide is reprecipitated from the solution of the cadmium ammonium compound.

3. **Alkali and Ammonium Carbonates** precipitate the white, basic carbonate insoluble in excess.

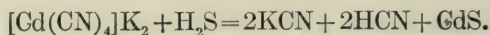
4. **Potassium Cyanide** precipitates white, amorphous cadmium cyanide,



readily soluble in excess:



From the solution of cadmium potassium cyanide the above-mentioned reagents produce no precipitation; but hydrogen sulphide decomposes it readily, forming a precipitate of yellow cadmium sulphide (difference from copper).





5. **Hydrogen Sulphide** produces precipitates varying in color from a canary-yellow, orange to almost brown, according to the conditions. In neutral solution, whether hot or cold, light-yellow cadmium sulphide is obtained in a condition hard to filter. From acid solutions (containing in 100 c.c. from 2 to 10 c.c. of conc.  $\text{H}_2\text{SO}_4$ , or from 2 to 5 c.c. of conc.  $\text{HCl}$ ) yellow precipitates which turn orange in color are at once thrown down and are easy to filter. The latter precipitates are not pure  $\text{CdS}$ , but always contain more or less  $\text{Cd}_2\text{Cl}_2\text{S}$  or  $\text{Cd}_2(\text{SO}_4)\text{S}$ . For this reason cadmium should not be determined quantitatively as the sulphide.

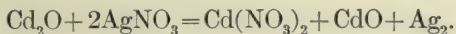
Cadmium sulphide is insoluble in alkaline sulphides (difference from arsenic), but is soluble in considerable hydrochloric acid, warm dilute nitric acid, and hot dilute sulphuric acid (difference from copper).

6. **Ammonium Sulphide** produces in ammoniacal solutions yellow colloidal cadmium sulphide, which has a tendency to pass through the filter. The presence of a concentrated salt solution prevents its doing this (cf. p. 164).

#### REACTIONS IN THE DRY WAY.

Cadmium compounds, heated on charcoal with soda, give a brown incrustation of cadmium oxide.

If a compound of cadmium oxide is reduced in the upper reducing flame of the Bunsen burner, the cadmium oxide is changed to metal, which volatilizes, and, in the upper oxidizing flame, goes back to oxide, which will be deposited as a brown coating if a glazed porcelain dish filled with water is held just above the flame. This oxide always contains some suboxide mixed with it, and has the property of reducing silver oxide to metal; so that if the coating of oxide is moistened with silver nitrate solution a black deposit of metallic silver will be obtained:



This reaction is very sensitive.

If it is desired to test the precipitate produced by hydrogen sulphide for cadmium in this way, the sample is first roasted in the oxidizing flame and then treated as just described.

## SEPARATION OF MERCURY, LEAD, COPPER, BISMUTH, AND CADMIUM FROM THE PREVIOUS GROUPS AND FROM ONE ANOTHER.

In order to separate these metals from the previous groups, the solution is acidified with hydrochloric acid \* (for 100 c.c. of solution, 10 to 15 c.c. of double normal acid should be used) and saturated with hydrogen sulphide in the cold; then diluted with an equal volume of water,† again saturated with hydrogen sulphide, filtered and washed with water containing hydrogen sulphide.

The precipitate thus obtained contains mercury, lead, copper, bismuth, and cadmium as sulphides, and may be analyzed according to Table V, page 207. The filtrate from the hydrogen sulphide precipitate contains the members of the previous groups.

The following metals are also precipitated from acid solutions by hydrogen sulphide, but their sulphides are sulphoanhydrides, and are, therefore, soluble in alkali sulphides, forming sulpho salts.

To this group belong arsenic, antimony, tin (gold, platinum, tungsten, molybdenum, vanadium, selenium, and tellurium).

### ARSENIC, As. At. Wt. 74.96.

Sp. Gr. = 5.73.

*Occurrence.*—Arsenic is widely distributed in nature, being found in small amounts in almost all sulphides, as, for example, sphalerite and pyrites: therefore almost all the zinc and sulphuric acid of commerce contain arsenic.

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\* Nitric acid is used only when lead is present, which can always be determined by the preliminary examination; in all other cases it is far better to acidify with hydrochloric or sulphuric acid (cf. p. 9). The reason so much acid is used is to prevent the precipitation of zinc. In the presence of much copper and little zinc, hydrogen sulphide precipitates all of the zinc as sulphide if the solution is only slightly acid with mineral acids; if, however, enough acid is present, none of the zinc will be precipitated. After all the copper has been precipitated, the zinc will not be precipitated by dilution with water and treatment with more hydrogen sulphide.

† The above mentioned dilution with water is in all cases necessary, as cadmium will otherwise (often) not be precipitated, and will come down on adding ammonium sulphide with the members of Group III. If the solution is diluted as above, all the cadmium will be precipitated.

TABLE V. SEPARATION OF MERCURY, LEAD, COPPER, BISMUTH, AND CADMIUM.

The sulphides obtained by hydrogen sulphide ( $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{CdS}$ ) are treated in a porcelain dish with nitric acid (sp. gr. 1.2) and warmed; all of the sulphides dissolve except  $\text{HgS}$ . The residue is filtered off and washed with water.

RESIDUE ( $\text{HgS}$ ).

Dissolve in aqua regia, evaporate almost to dryness, add water and filter off any sulphur.

Add stannous chloride to the filtrate; a white precipitate of  $\text{Hg}_2\text{Cl}_2$ , which, on further addition of  $\text{SnCl}_2$ , becomes gray, shows mercury.

Evaporate to a small volume, add a few cubic centimeters of dilute sulphuric acid,\* evaporate until fumes of sulphuric acid come off, cool, dilute with a little water,† and filter.

RESIDUE ( $\text{PbSO}_4$ ).

The formation of a white residue of  $\text{PbSO}_4$  shows lead. It is confirmed by the charcoal-stick test; a malleable button, soluble in nitric acid, shows lead.

The solution is saturated with ammonia and filtered.

RESIDUE ( $\text{BiSO}_4\text{OH}$ )

The white precipitate shows bismuth if the analysis has been done correctly.‡ It is confirmed (always) by washing the precipitate, dissolving in a little  $\text{HCl}$ , and adding an alkaline solution of potassium stannite. A black precipitated metallic bismuth shows bismuth.

SOLUTION [ $\text{CuSO}_4$ ,  $\text{Bi}_2(\text{SO}_4)_3$ ,  $\text{CdSO}_4$ ].

A blue solution shows copper.

KCN is added until the solution is decolorized, and hydrogen sulphide is passed into the solution; a yellow precipitate shows cadmium.§

Cadmium is confirmed by the flame reaction. A little of the filtered and washed precipitate is placed on an asbestos thread, roasted carefully in the upper oxidizing flame, and the oxide incrustation produced on a porcelain dish (see p. 205).

On moistening the brown coating with silver nitrate it becomes bluish-black if cadmium is present.

\* If considerable lead is present, the addition of dilute sulphuric acid produces a precipitate immediately. If only little lead is present, the precipitate appears only after evaporation and dilution (see p. 188).

† Too much water should not be added, otherwise basic bismuth sulphate may be precipitated.

‡ A white or brown precipitate of  $\text{Al}(\text{OH})_3$  or  $\text{Fe}(\text{OH})_3$  is often obtained here, if the precipitate produced by hydrogen sulphide was incompletely washed.

§ If much copper is present, a red precipitate of  $(\text{CSNH}_2)_2$  is sometimes obtained (see p. 201).



Arsenic occurs native in kidney-shaped masses; also in the form of its oxide,  $\text{As}_2\text{O}_3$ , as isometric arsenolite and orthorhombic claudetite, it being dimorphous.

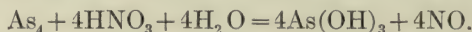
Mimetite,  $(\text{AsO}_4)_3\text{Pb}_5\text{Cl}$ , hexagonal, isomorphous with apatite, pyromorphite, and vanadinite, is a well-known mineral containing arsenic oxide.

The most important sources of arsenic are the sulphides, arsenides, and sulpho salts: realgar,  $\text{As}_2\text{S}_2$ , monoclinic; orpiment,  $\text{As}_2\text{S}_3$ , monoclinic; arsenopyrite,  $\text{FeAsS}$ , orthorhombic; niccolite,  $\text{NiAs}$ , hexagonal; löllingite,  $\text{FeAs}_2$ , orthorhombic; smaltite,  $(\text{Co}, \text{Ni}, \text{Fe})\text{As}_2$ , isometric; and proustite,  $\text{As}(\text{SAg})_3$ , rhombohedral.

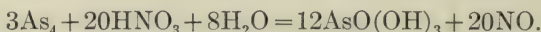
Metallic arsenic is a steel-gray, brittle substance. On being heated it sublimes, giving off a characteristic garlic odor. The merest trace of arsenic may be recognized by this odor. The molecule of arsenic contains, like phosphorus, four atoms,  $(\text{As}_4)$ .

Arsenic is insoluble in hydrochloric acid, but readily soluble in nitric acid and in aqua regia.

Dilute nitric acid dissolves arsenic, forming arsenious acid:

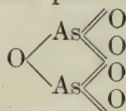
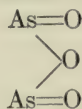


Concentrated nitric acid and aqua regia dissolve it, forming arsenic acid:



Arsenic belongs to the same natural group of elements as nitrogen and phosphorus, and forms, as they do, two oxides.

Arsenic trioxide \* and Arsenic pentoxide



which almost always act as acid anhydrides.

#### A. Arsenious Compounds.

Arsenic trioxide is formed by the combustion of arsenic in the air as white, glistening crystals of regular octahedrons. If the vapors of the trioxide are allowed to cool slowly, they solidify to an

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\* In reality the symbol is  $\text{As}_4\text{O}_6$ , but it is customary to use the simpler symbol,  $\text{As}_2\text{O}_3$ .

amorphous glass (arsenic glass), which gradually becomes crystalline (white and opaque, like porcelain).

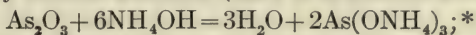
Arsenic trioxide is known in three different modifications:

1. Isometric arsenic trioxide, white arsenic;
2. Monoclinic arsenic trioxide, and
3. Amorphous, glassy arsenic trioxide.

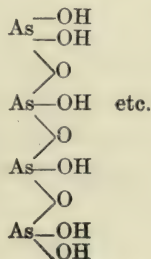
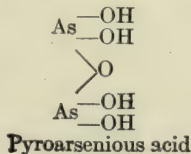
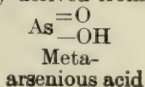
The monoclinic modification is difficultly soluble in water (80 parts of cold water dissolve one part of  $\text{As}_2\text{O}_3$ ); while the amorphous, glassy modification is much more soluble (25 parts of cold water dissolve one part of arsenic trioxide). By treatment of the ordinary modification (white arsenic) with water, it is not wet by the latter, appearing like meal, which is very characteristic.

The trioxide dissolves quite readily in hydrochloric acid, particularly on warming, from which solution it often separates out, on cooling, in a beautiful, crystalline, anhydrous condition.

Acting as an acid anhydride it dissolves readily in alkalis, forming easily soluble arsenites (salts of arsenious acid):



\* The tri-metal arsenites derived from the ortho acid  $\text{As} \begin{smallmatrix} \text{OH} \\ \text{OH} \\ \text{OH} \end{smallmatrix}$  are usually unstable. Only the silver salt  $\text{As} \begin{smallmatrix} \text{OAg} \\ \text{OAg} \\ \text{OAg} \end{smallmatrix}$  is well known. The alkali arsenites are really derived from

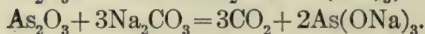
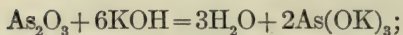


With sodium and potassium, only the two following types are known:



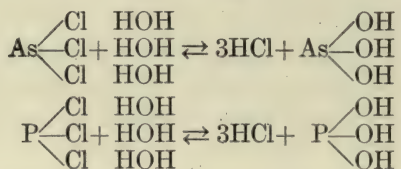
With ammonium, only the ammonium pyroarsenite,  $\begin{array}{c} \text{As}=(\text{ONH}_4)_2 \\ \diagup \text{O} \diagdown \\ \text{As}=(\text{ONH}_4)_2 \end{array}$ , is known.

The salts,  $\text{As} \begin{smallmatrix} =\text{O} \\ -\text{OK} \end{smallmatrix}$  and  $\text{As} \begin{smallmatrix} =\text{O} \\ -\text{ONa} \end{smallmatrix}$ , in alkaline solution behave as salts of the ortho acid:  $\text{As}(\text{OK})_3$  and  $\text{As}(\text{ONa})_3$ .



Free arsenious acid,  $\text{As(OH)}_3$ , has never been isolated; as a very weak acid it breaks down, like carbonic acid, into water and the anhydride.

Arsenic combines with chlorine directly, like phosphorus, forming the chloride,  $\text{AsCl}_3$ , which behaves exactly like the chloride of arsenious acid, similar to  $\text{PCl}_3$ . It is a colorless liquid, boiling at  $134^\circ \text{C}$ ., and is decomposed quantitatively, like all acid chlorides, with water:



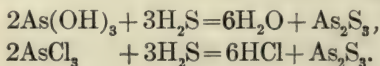
The aqueous solution of arsenic trichloride, and the solution of the trioxide in dilute hydrochloric acid, contain the arsenic as arsenious acid.

As the concentration of the hydrochloric acid increases, the amount of arsenic trichloride increases, until in very concentrated hydrochloric acid the arsenic is present almost entirely as trichloride. By boiling a solution of arsenic trichloride in hydrochloric acid, arsenic trichloride is given off as a gas. If hydrochloric acid is conducted into the solution at the same time (so that the concentration of the hydrochloric acid is kept as large as possible), all the arsenic can be volatilized from the solution as arsenious chloride. On evaporating a hydrochloric acid solution of arsenious acid, arsenious chloride constantly escapes, so that all the arsenic may be volatilized. If, however, the arsenic is present in the form of arsenic acid, no arsenic is lost during the evaporation of the solution.

#### REACTIONS OF ARSENIUS ACID IN THE WET WAY

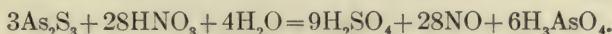
The arsenites of the alkalis are soluble in water; the remaining arsenites are insoluble in water, but soluble in acids.

1. **Hydrogen Sulphide** precipitates from acid solutions yellow flocculent arsenic trisulphide:

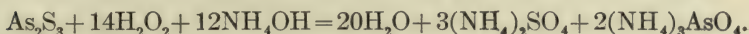




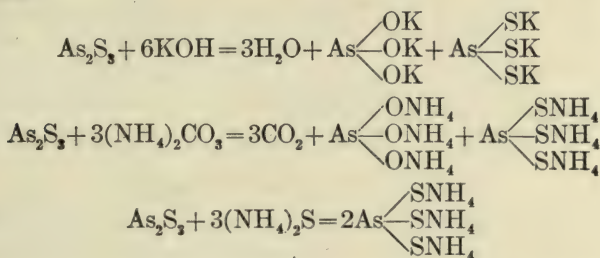
Arsenious sulphide is insoluble in acids; even quite concentrated boiling hydrochloric acid \* (1:1) does not dissolve it. Concentrated nitric acid oxidizes it to arsenic acid and sulphuric acid:



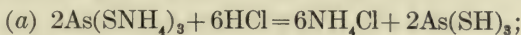
The sulphide is more soluble in ammoniacal hydrogen peroxide:



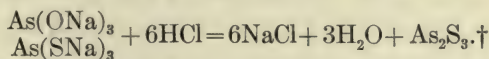
It is also dissolved by alkalies, ammonium carbonate, and alkali sulphides:



Just as the anhydride,  $\text{As}_2\text{O}_3$ , can be referred to the acid,  $\text{As}(\text{OH})_3$ , so the sulphoanhydride,  $\text{As}_2\text{S}_3$ , can be referred to the sulphoarsenious acid,  $\text{As}(\text{SH})_3$ , which is not capable of existence in the free state, but is known in the form of its salts. If one of the latter salts is acidified, then sulphoarsenious acid is set free; but it immediately loses  $\text{H}_2\text{S}$ , forming the insoluble sulphoanhydride:



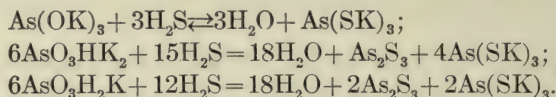
On treating a mixture of sulpho- and oxyarsenites with acid, arsenic trisulphide is also precipitated:



\* By long heating with concentrated hydrochloric acid, it is slowly changed to volatile  $\text{AsCl}_3$  and  $\text{H}_2\text{S}$ .

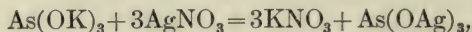
† The precipitation is quantitative only when the solution is dilute; from a concentrated solution  $\text{H}_2\text{S}$  escapes, so that more  $\text{H}_2\text{S}$  must be conducted into the solution in order to precipitate all the arsenic.

This property of forming sulpho-salts accounts for the fact that hydrogen sulphide produces no precipitation from normal arsenites, and only a partial precipitation of  $\text{As}_2\text{S}_3$ , from mono- and dimetallic salts:

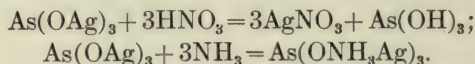


Consequently, in order to precipitate arsenic completely as trisulphide, it is always necessary that the solution should contain enough free acid to prevent the formation of soluble sulpho-salts.

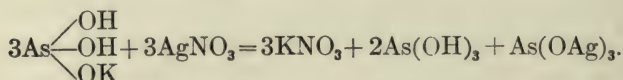
2. **Silver Nitrate** produces in neutral solutions of arsenites a yellow precipitate of silver orthoarsenite (difference from arsenic acid):



soluble in nitric acid and ammonia:

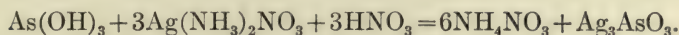


The normal (ortho) arsenites are unknown in the solid state; only the meta- and pyroarsenites have been isolated (cf. page 209, foot-note), which behave in aqueous solutions as acid salts of the ortho-acid. Consequently, silver nitrate produces only an incomplete precipitation in aqueous solutions of the mono- and dimetallic salts:



In order to make the precipitation quantitative, an alkali (preferably ammonia) must be added. As, however, the solution already reacts alkaline, it is difficult to reach the exact neutral point. Usually too much alkali is added. It is, therefore, more practicable (if it is desired to make the precipitation quantitative) to add the ammonia to the silver nitrate until the precipitate of silver oxide just dissolves; but as a rule this is unnecessary, as it is only needful to observe the *color* of the precipitate in order to determine whether an arsenite or arsenate is present. If, however, the arsenite solu-

tion is made weakly acid with nitric acid,\* and the silver nitrate solution (which has been treated with ammonia) is then added, the arsenite will be, practically, completely precipitated, even if an excess of the reagent is employed:

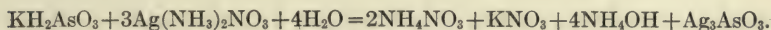


In case the solution to be tested contains also a chloride, it should be acidified with nitric acid and the chloride precipitated as silver chloride by an excess of silver nitrate, and filtered off. To the filtrate, dilute ammonia should be cautiously added. At the neutral zone formed by the ammonia above the acid solution, a yellow precipitate of silver arsenite will appear. This reaction is very sensitive.

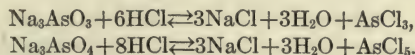
3. **Magnesium Ammonium Chloride** produces no precipitation in dilute arsenite solutions in the presence of ammonia (difference from arsenic acid).

4. **Iodine Solution** is decolorized by arsenious acid, the latter being oxidized to arsenic acid; the reaction does not take place quantitatively in acid solution:†

\* As otherwise the solution will become ammoniacal, dissolving a part of the silver arsenite:

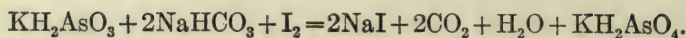


† In alkaline solutions, or in solutions kept nearly neutral by the presence of an excess of sodium bicarbonate, the arsenite ion is easily oxidized to the arsenate ion and the arsenic is increased in valence from three to five. In acid solutions, however, there is, at least to some extent, a decomposition of the arsenite into trivalent arsenic ions and of the arsenate into quinquevalent arsenic ions and the latter are easily reduced to the trivalent condition.



Thus iodine oxidizes an arsenite quantitatively in a neutral solution and conversely an arsenate is quantitatively reduced by potassium iodide in a strongly acid solution. This behavior is often attributed to the free hydriodic acid possessing a stronger reducing power than the iodine ion in an iodide, but probably the effect of the acid upon the arsenate is the true explanation; the quinquevalent arsenic ion has a much greater oxidizing power than the arsenate ion because the former is not very stable.

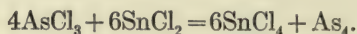




The solution must be neutralized with sodium bicarbonate and not with normal sodium hydroxide, because the latter also decolorizes iodine:

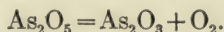


**5. Stannous Chloride (Bettendorff's Test).**—On adding to concentrated hydrochloric acid a few drops of an arsenite solution and then  $\frac{1}{2}$  c.c. of a saturated solution of stannous chloride in hydrochloric acid, the solution quickly becomes brown and then black, owing to the deposition of metallic arsenic. The reaction takes place more readily on warming, but a dilute aqueous solution will not give the reaction. In concentrated hydrochloric acid, however, the arsenic is all present as trichloride, and this is reduced by the stannous chloride, while arsenious acid is not:

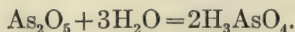


### B. Compounds of Arsenic Pentoxide.

Arsenic pentoxide, which may be obtained by heating arsenic acid, is a white, fusible substance, and is changed by strong ignition into arsenic trioxide:



Arsenic pentoxide is quite soluble in water, forming arsenic acid:



Arsenic acid itself may be obtained in the solid state in the form of orthorhombic prisms corresponding to the formula  $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ . At  $100^\circ$  C. water escapes, orthoarsenic acid,  $\text{H}_3\text{AsO}_4$ , being left behind as a crystalline powder.

By gentle ignition more water is given off, forming pyroarsenic acid,  $\text{H}_4\text{As}_2\text{O}_7$ , which on further ignition is changed to metarsenic

acid,  $\text{HAsO}_3$ . In this respect arsenic acid acts exactly like phosphoric acid. Both the pyro- and the meta-acids readily take on water, and are changed back to the ortho acid.

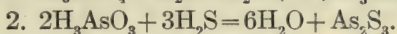
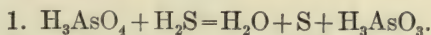
The salts of arsenic acid are called arseniates.

As with orthophosphoric acid, mono-, di-, and trimetallic salts are known:  $\text{NaH}_2\text{AsO}_4$ ,  $\text{Na}_2\text{HAsO}_4$  and  $\text{Na}_3\text{AsO}_4$ .

The arseniates of the alkalies are soluble in water; the others are insoluble in water but easily soluble in acids.

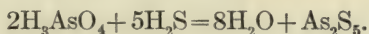
#### REACTIONS IN THE WET WAY.

**1. Hydrogen Sulphide.**—If hydrogen sulphide is conducted into a cold, fairly acid solution of arsenic acid, the liquid remains clear for a long time; it gradually becomes turbid, the arsenic acid being reduced to arsenious acid with deposition of sulphur, and the arsenious acid is then quickly precipitated as trisulphide:



If hydrogen sulphide is passed into the same solution after it has been heated, the reduction takes place more rapidly and the arsenious sulphide, therefore, is more readily formed.

In the presence of *considerable hydrochloric acid*, and by passing hydrogen sulphide rapidly into the *cold* solution, all the arsenic is precipitated as arsenic pentasulphide:

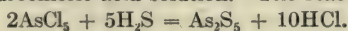


If a fairly concentrated hydrochloric acid solution is treated while hot with hydrogen sulphide, a mixture of tri- and pentasulphides is obtained.

This peculiar behavior may be explained by assuming that the solution in concentrated hydrochloric acid contains the arsenic as pentachloride,\* which is not reduced readily by hydrogen sulphide, so that arsenic pentasulphide is precipitated; while on addition of water the pentachloride is changed to arsenic acid, which is re-

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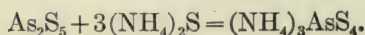
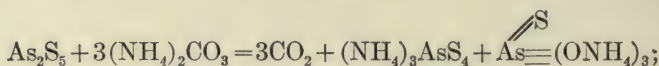
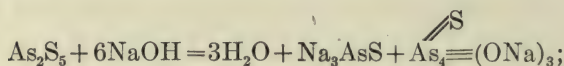
\* Arsenic pentachloride has never been isolated; but it is possible that it can exist only in hydrochloric acid solution. The reaction would then be



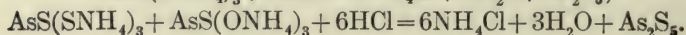
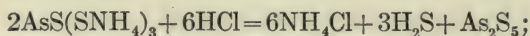
duced by hydrogen sulphide to arsenious acid before it is precipitated.

To precipitate the arsenic quickly by hydrogen sulphide from a solution of arsenic acid, or an arseniate, without employing considerable hydrochloric acid, it is only necessary to reduce the arsenic acid, by boiling with sulphurous acid, to boil off the excess of the latter, and then to conduct hydrogen sulphide into the solution, whereby a precipitate of arsenious sulphide is at once formed.

Arsenic pentasulphide, like the trisulphide, is insoluble in boiling concentrated hydrochloric acid, but readily soluble in alkalis, ammonium carbonate, and alkali sulphides:



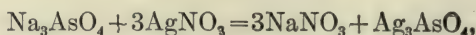
By acidifying these solutions, arsenic pentasulphide is reprecipitated:



Arsenic pentasulphide is oxidized by fuming nitric acid to sulphuric and arsenic acids; also by solution in ammoniacal hydrogen peroxide:



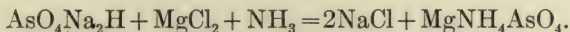
**2. Silver Nitrate** precipitates from neutral solutions chocolate-brown silver arseniate (difference from arsenious and phosphoric acids):



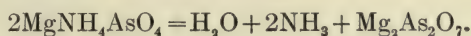
soluble in acids and in ammonia.



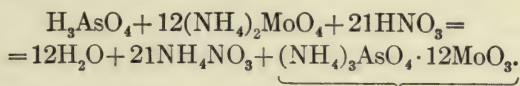
3. **Magnesium Chloride** precipitates, in the presence of ammonia and ammonium chloride, a white, crystalline precipitate of magnesium ammonium arseniate:



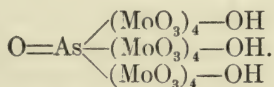
This precipitate is insoluble in ammonia water and is used for the quantitative determination of arsenic. By ignition it is changed into magnesium pyroarsenate:



4. **Ammonium Molybdate** in considerable excess precipitates, in a boiling nitric acid solution, yellow crystalline ammonium arsenomolybdate:



Arsenic acid, like phosphoric acid, forms with molybdic acid a tribasic complex acid, the arsenomolybdic acid, of the structure



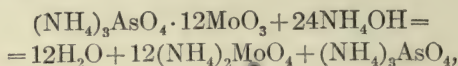
This tribasic acid is soluble in nitric acid, but the ammonium and potassium salts are insoluble.

The solution of ammonium molybdate for use as a reagent may be prepared as follows: 150 grams of commercial ammonium molybdate,  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 4\text{H}_2\text{O}]$ , are dissolved in a liter of distilled water and poured into a liter of nitric acid (sp. gr. 1.2). At first white molybdic acid will be precipitated, but this dissolves finally in the nitric acid, forming a clear solution.

If arsenic acid is added to this solution, the soluble arsenomolybdic acid is first formed, which immediately reacts with the ammonium nitrate present (formed from the ammonium molybdate and nitric acid), producing the insoluble ammonium salt of the arseno-molybdic acid.

But this ammonium salt is soluble in a solution containing an alkali arseniate, forming complex acids containing more arsenic in the molecule, whose ammonium salts are soluble in nitric acid. Consequently a large excess of ammonium molybdate should be used if it is desired to precipitate arsenic acid.\*

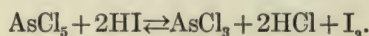
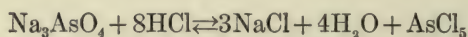
The ammonium salt of arseno-molybdic acid is also readily soluble in alkalies and in ammonia:



from which solution arsenic acid may be precipitated as white crystalline magnesium ammonium arseniate.

As we shall see later, phosphoric acid behaves similarly towards magnesium salts and ammonium molybdate. If, therefore, phosphoric acid and arsenic acid are both present, it is necessary to precipitate first the arsenic with hydrogen sulphide, filter, and oxidize the precipitated arsenic sulphide to arsenic acid with fuming nitric acid. In such a solution a precipitate produced by means of ammonium molybdate or magnesium chloride must be caused by arsenic acid. In the same way a precipitate produced *in the filtrate* from the hydrogen sulphide precipitate must be caused by phosphoric acid.

5. **Potassium Iodide**, in a solution strongly acid with hydrochloric acid, reduces a solution of an arsenate with liberation of iodine;



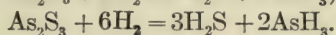
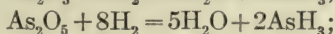
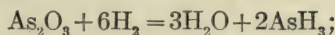
The reaction takes place quantitatively if the iodine is removed by adding sodium thiosulphate. See page 213, foot-note.

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\* The addition of a concentrated ammonium nitrate solution increases the sensitiveness of this reaction.

### C. Reactions which may be obtained with either Arsenious or Arsenic Compounds.

1. **The Berzelius-Marsh Test for Arsenic.**—All compounds containing arsenic may be reduced, in acid solution, by means of nascent hydrogen to arsine,  $\text{AsH}_3$ :



The sulphides are reduced very slowly, but the oxides are reduced quickly even at ordinary temperatures. To produce nascent hydrogen, zinc and sulphuric acid are used.

This *very* poisonous arsine possesses a property which enables us to detect with certainty the merest trace of arsenic—as little as 0.0007 milligram As. By conducting the gas through a heated glass tube filled with hydrogen, it is decomposed into hydrogen and metallic arsenic; and the latter is deposited as a brownish-black mirror on the sides of the glass tube, just beyond the place where it was heated.

This test is extremely sensitive, and must be made with great precaution, as almost all reagents, especially commercial zinc and sulphuric acid, are likely to contain traces of arsenic. In case these are used without previous testing, arsenic is likely to be found even although it may not have been present in the substance itself.

The Marsh test is particularly useful for detecting the presence of very small amounts of arsenic which could not be found by any of the previously-mentioned reactions. In cases of poisoning, and for detecting the presence of arsenic in wall-papers, this test, or a modification of it, is always used; we will, therefore, discuss it in detail.

#### *Formation and Properties of Arsine.*

(a) *Formation.*—Arseniuretted hydrogen, or arsine, is produced, as above mentioned, by the reduction of compounds containing arsenic by means of nascent hydrogen. For developing the latter pure zinc and pure sulphuric acid should be used. If other metals and other acids are used (*e.g.*, tin and hydrochloric acid, iron and



sulphuric acid), the arsenic compound will be reduced; but if iron is used, a part of the arsenic is changed to solid arseniuretted hydrogen, which remains in the flask and consequently escapes detection. If tin and hydrochloric acid are used, a high temperature is necessary in order to accomplish the reduction;\* while with zinc and sulphuric acid the reaction takes place readily at the ordinary temperature. Chemically pure zinc dissolves with difficulty in chemically pure sulphuric acid, so that it is well to activate the zinc by the addition of a little foreign metal. The addition of a drop of chloroplatinic acid causes at first a more rapid evolution of hydrogen, but the reaction soon slows down and is not accelerated by the addition of more chloroplatinic acid. Moreover, the addition of chloroplatinic acid has the disadvantage of causing considerable arsenic to be held back by the platinum; less than 0.005 mgm. of  $\text{As}_2\text{O}_3$ , cannot be detected in this way.† Much better results are obtained by using an alloy of zinc and platinum. Thus F. Hefti‡ found that zinc alloyed with 10 per cent platinum caused a more uniform evolution of hydrogen and that the formation of arsine was accelerated while less arsenic was retained by the platinum. With this alloy quantities of  $\text{As}_2\text{O}_3$  as small as 0.0005 mgm. can be detected with certainty. The best activating agent, however, is copper in the form of a zinc-copper alloy prepared as follows: Twenty grams of the purest zinc are melted in a small Hessian crucible. A little pure copper is added and stirred into the molten zinc with a stick of zinc. The metal is then granulated by pouring it into water, keeping as much as possible of the oxide back in the crucible. With this alloy and 15 per cent sulphuric acid, a steady continuous current of gas is obtained and it is possible to detect with certainty as little as 0.00025 mgm. of  $\text{As}_2\text{O}_3$ .

Arsenic, arsenious oxide, arsenic pentoxide, and arsenic trisulphide are readily reduced in alkaline solution by sodium amalgam, aluminium, or Devarda's alloy and caustic potash, forming arsine. The reduction takes place quickly, and the arsine may be detected

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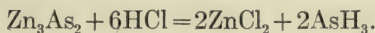
\* Thus Vanino, working at ordinary temperatures, could not detect less than 0.002 gm. of  $\text{As}_2\text{O}_3$  by means of tin and hydrochloric acid, and where chloroplatinic acid was added, less than  $\frac{1}{10}$  mgm. of  $\text{As}_2\text{O}_3$  could not be found. *Z. angew. Chem.* 1902, 82.

† Bernstein, *Inaug.-Dissert.*, Rostock, 1870. ]

‡ *Inaug.-Dissert.*, Zürich, 1907.

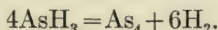
by the Gutzeit reaction (cf. p. 227). The presence of organic matter in solution hinders the reaction; 3 c.c. of urine in which 1 mgm. of  $\text{As}_2\text{O}_3$  was dissolved showed no trace of arsine after treating for hours with Devarda's alloy and caustic potash solution. In such cases the organic substance must be decomposed before testing for arsenic. (Cf. pages 225 and 227.)

Arsine is also obtained by dissolving many arsenides in hydrochloric or sulphuric acid:

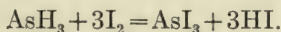


The arsenides of iron are attacked by acids only with difficulty, except when an excess of iron is present, when, with the help of the nascent hydrogen, they are decomposed, forming solid and gaseous arseniuretted hydrogen. Consequently iron sulphide containing arsenic, on treatment with acids, always yields hydrogen sulphide contaminated with arsine.\*

(b) *Properties*.—Arsine is a colorless, unpleasant-smelling, extremely poisonous gas, which, on being heated away from the air, is decomposed into arsenic and hydrogen:



By heating in the air, it is oxidized to water and arsenic trioxide. Solid iodine changes it to arsenious iodide and hydriodic acid:



This reaction takes place on conducting arsine over solid iodine. *This property serves to free hydrogen sulphide from arsine*, as hydrogen sulphide does not act upon solid iodine, but only upon aqueous iodine solutions. Arsine is not attacked by hydrogen sulphide at ordinary temperatures, but at  $230^\circ\text{C}$ . sulphide of arsenic and hydrogen are formed.

Arsine is a strong reducing agent: silver salts are reduced to metal (see page 227).

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\* Certain microbes, namely, *Penicillium brevicaulis*, when provided with nutriment containing only traces of arsenic, have the power of forming volatile arsenic compounds of a garlic odor, and this may be used as an extremely sensitive test for arsenic. (Chem. Zentralbl., 1902, I. p. 1245.)

### Directions for Performing the Berzelius-Marsh Test.

The apparatus devised by G. Lockemann,\* shown in Fig. 20, may be used to advantage.

In the flask K, of 100 to 150 c.c. capacity, there is placed three or four grams of zinc alloyed with copper† and about 20 c.c. of sulphuric acid free from arsenic (1 vol. conc.  $\text{H}_2\text{SO}_4$  diluted with 8 vols. of water). A steady stream of hydrogen is at once evolved, and in twenty minutes the air will be entirely driven out of the apparatus. When, at the end of about twenty minutes, the

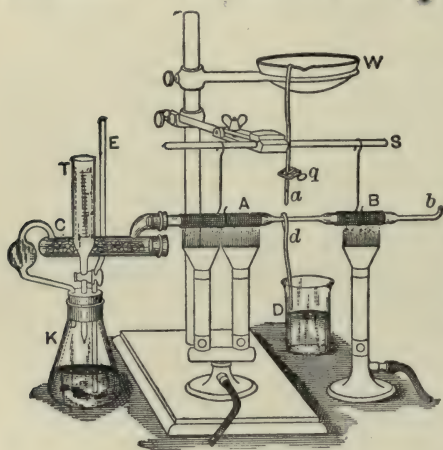


FIG. 20.

gas escaping at *b* is found to be pure (by collecting a little in a small tube and holding it near a flame; it should light without a sharp explosion) the hydrogen is lighted at *b*.‡ The flame will be about two or three millimeters high and should remain so during the whole of the experiment; if it becomes higher the solution in K is cooled by placing the flask in cold water, and, conversely, when the flame is too low

a little sulphuric acid is added, or the flask is placed in warm water.

First of all the reagents, zinc and sulphuric acid, are tested to see that they are free from arsenic. The hard-glass tube is heated at B just before the restriction in the tube, which is 5 mm. long and 1.5–2 mm. wide. If at the end of twenty minutes there is no arsenic

\* *Z. angew. Chem.*, 1905, pp. 427 and 491.

† Melt 20 grams of zinc (free from arsenic) with a trace of pure copper and pour the fusion into cold water.

‡ A safe way to light the flame is to take the small tube used for testing the gas, fill it with gas, light it, and bring it to the end of the tube *b*. If the gas is pure the hydrogen in the small tube will burn quietly for some little time. If impure, there will be none left in the small tube after it is exploded and this will not light the escaping gas at *b*.



mirror formed in this capillary, the reagents are free from arsenic.

The sulphuric acid solution to be tested for arsenic, and which must be free from organic substances, sulphides, chlorides, nitrates, or other oxidizing agent, is then placed in the graduated funnel T, and is added little by little to the flask K without in any way interrupting the current of hydrogen. Just before adding the solution to the flask, the two burners at A are lighted and the glass tube thereby heated to dull redness. The gas as it escapes from the flask K passes through the drying-tube C containing crystallized calcium chloride, and then passes into the tube A, where any arsine is quantitatively decomposed into arsenic and hydrogen. The arsenic is deposited on the cold walls of the capillary. The end of the capillary is cooled in order to form a sharply defined mirror by winding around it a piece of wicking, as shown in Fig. 20, and allowing water to drop upon it from the dish W during the experiment.

All the arsenic will be deposited at the end of an hour, and by comparing the mirror with a series of standards the amount can be estimated accurately (see page 226).

*Remark.*—If the tube A is not heated at all, but the gas ignited at *b* as above described, the arsenic may be deposited upon a cold porcelain dish by holding the dish in the flame. The deposit is readily soluble in sodium hypochlorite solution (difference from antimony). In this form the test was used by James Marsh in 1836.

*Confirmatory Test.*—

In the small glass tube open at both ends (see Fig. 21) is found in the

arsenic mirror. The tube is held in an inclined position and heated by means of a small flame whereby the arsenic is changed to arsenic trioxide, giving off the characteristic garlic odor, which

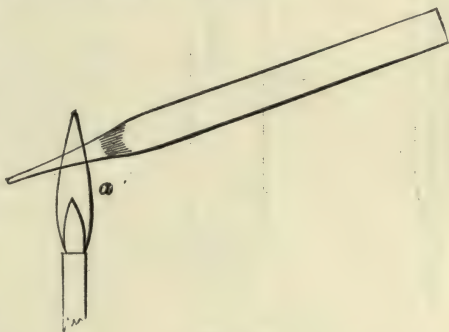


FIG. 21.

can be detected at the upper end of the tube if only  $\frac{1}{100}$  of a milligram of arsenic trioxide is formed. After the tube is cooled, the arsenic trioxide is to be found at *a* in the form of small glistening octahedrons, which can be seen with the magnifying glass or often with the naked eye.

These three facts—formation of the mirror, the garlic odor, and the octahedrons—suffice to make us sure of the presence of arsenic; but the more proofs we have, the more certain we are of the accuracy of the result. If the octahedrons have been recognized, the capillary end of the tube is sealed with a flame, and 1–2 drops

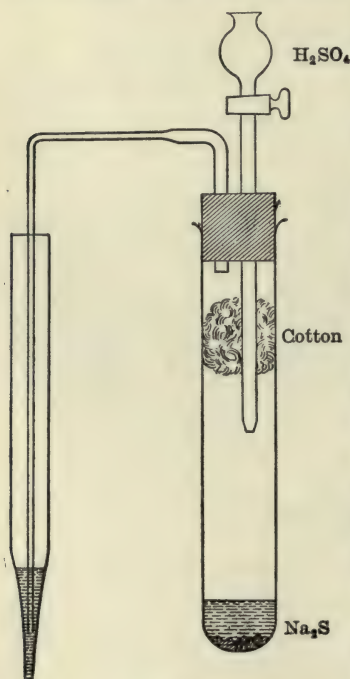


FIG. 22.

of pure concentrated hydrochloric acid are introduced into the tube with the help of a dropper, and the tube is moved so that the arsenic trioxide is moistened by the acid; 6–10 drops of distilled water are added and hydrogen sulphide is conducted into the tube, whereby yellow arsenious sulphide is formed.

The hydrogen sulphide in this case is generated from a solution of sodium sulphide by adding a little sulphuric acid, as illustrated in Fig. 22. The upper part of the test-tube contains a wad of cotton wool, which prevents any of the solution in the tube from being mechanically carried over into the tube containing the arsenic.

As an example of the practical application of this delicate test, we will describe the method to be employed in the detection of arsenic in wall-papers, etc. Many wall-papers contain small amounts of arsenic, and it is desired to know how much is present in a definite area of the paper, say a square meter. The amount of arsenic contained in wall-papers is usually so small that weighing the mirror produced would not be accurate. It is best, therefore, to prepare a number of mirrors from

known amounts of arsenic, to establish a scale for determining how much is contained in the given wall-paper or fabric.\*

We must first extract the arsenic without loss from the paper, and to this end it is necessary to decompose the organic material, which is accomplished preferably as follows:

### Decomposition of Organic Material.

Exactly one square decimeter (100 sq.cm.) of wall paper are rolled into a cylinder and introduced into a tube closed at one end, such as is used for the Carius determination of the halogens (see Volume II of this book). Two cubic centimeters of pure, fuming sulphuric acid (25 per cent. oleum, Kahlbaum) are added through a long-stemmed funnel. Then three or four cubic centimeters of fuming nitric acid are poured into a small test-tube and the latter is carefully allowed to slip down the sides of the Carius tube so that the two acids do not come in contact with one another. A thick capillary is drawn out and sealed as described in Volume II. The tube is enveloped in asbestos paper and slowly heated, in the furnace used for Carius tubes, to a temperature of about 230° and kept there for an hour and a half. The tube is allowed to cool and is withdrawn from the iron protective tube, by means of a wire previously fastened to it, until the capillary projects a little, and this is heated with a Bunsen flame. As soon as the glass becomes soft the pressure on the inside of the tube blows out a hole through which gas escapes until the pressure is the same inside the tube as without. The point of the tube is then broken off and the contents of the tube and of the tip are rinsed into a porcelain evaporating dish. The colorless solution † thus obtained will contain all the arsenic in the form of arsenic acid. The solution is evaporated till fumes of sulphuric acid are evolved thickly, and then, after cooling, 15 c.c. of water are added and the liquid poured into the funnel T of Fig. 20, and the dish is rinsed twice, each time with 3 c.c. of water. After mixing the liquid in T by means

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\* C. R. Sanger, Amer. Acad. of Arts and Sciences, 26, 24.

† If the paper contained iron or aluminium compounds, the anhydrous sulphates are formed. These dissolve by heating with water. The above method is the best and cleanest for decomposing organic material.



of a small stirring rod, the total volume of the liquid is noted.\* During this operation, the Marsh apparatus should be made ready for the test.

A few drops of the well-mixed solution are now added through T to the reduction flask K. If no mirror appears within three or four minutes,  $\frac{1}{8}$  to  $\frac{1}{4}$  of the filtrate is added little by little; and if no mirror appears after five minutes, the whole filtrate. The whole filtrate is not added at once, because if too strong a mirror is obtained, it is much more difficult to estimate the amount of arsenic present. After twenty-five minutes all the arsenic will be deposited if not more than 0.05 milligram of arsenic are in solution. If a mirror of sufficient density was obtained in fifteen minutes from only a fraction of the whole solution, no more should be added, but the operation should be continued for ten minutes more, the flame extinguished, and the tube allowed to cool while hydrogen continues to pass through it. The mirror is then compared with the scale, and the remaining part of the filtrate is weighed in order to determine how much was used for the test.

If sufficient material is at hand, a duplicate experiment should be made with a new tube and a new sample. The results of a few such determinations are given in the following table:

Cm. <sup>2</sup> of Paper used.	Weight of Extract.	Wt. of Extract taken.	Weight of Mirror.	Total Weight of As <sub>2</sub> O <sub>3</sub> in Extract.	Mg. As <sub>2</sub> O <sub>3</sub> per m. <sup>2</sup>
100	31.63	31.63	0	0	0
100	30.11	10.23	0.015	0.044	4.4
		9.87	0.013	0.0399	3.99
100	28.72	8.32	0.045	0.155	15.5
		7.53	0.042	0.163	16.3
50	30.22	2.64	0.015	0.172	34.4
		3.22	0.020	0.187	37.4

The comparison of the mirrors is best made in transmitted light. The normal mirrors are prepared as follows: 1 gram of pure sublimed arsenic trioxide is dissolved in a little sodium carbonate solution, acidified with dilute sulphuric acid, and diluted to a liter. Ten c.c. of this solution, of which 1 c.c. contains 1 milligram of As<sub>2</sub>O<sub>3</sub>,

\* Instead of measuring the liquid it may be weighed.

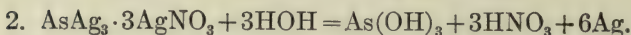
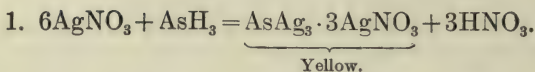
are again diluted to a liter, so that a solution is now obtained of which 1 c.c. contains 0.01 mg. of  $\text{As}_2\text{O}_3$ . One c.c., 2 c.c., 3 c.c., 4 c.c., and 5 c.c. are taken from the solution and introduced separately into the Marsh apparatus, and the corresponding mirrors are obtained in different tubes. Two tubes are made from each amount of arsenic, as the mirrors are not always the same. These mirrors may be kept in the dark for some time; but on exposure to the light they fade perceptibly. Mirrors which are sealed up with hydrogen do not keep as well.

### **Testing Urine, Blood, Milk, Beer, etc., for Arsenic.**

100 c.c. of the liquid in question are evaporated to dryness in a porcelain dish. The residue is introduced by means of a spatula as completely as possible into a tube, such as is used for the Carius determination (Vol. II), and 4 c.c. of a 25 per cent. oleum are added. In order to transfer the rest of the residue to the tube, 2 c.c. of fuming nitric acid are poured into the dish and after wetting all the sides of the dish, the acid is transferred to a small test-tube. This operation is repeated twice more and then the small test-tube is allowed to slip into the Carius tube. A capillary is drawn out at the open end of the tube and sealed by the flame. The tube is then heated in the Carius furnace for one hour at  $160^\circ$ . After cooling, the point of the tube is opened, with the usual precautions, and the pressure released. The tube is again sealed and heated for half an hour to an hour at  $230^\circ$ . The operation is then continued as described above.

With urine a somewhat different procedure is followed. The liquid is evaporated not quite to dryness but to sirupy consistency; the syrup is spread upon a porcelain boat and allowed to slip into the Carius tube. The rest of the process is carried out as before.

**2. The Gutzeit Test for Arsenic** depends upon the behavior of arseniuretted hydrogen towards a concentrated solution of silver nitrate (1:1) (according to Eidenbenz, a crystal of solid silver nitrate should be used). The silver nitrate is at first colored yellow and then black, the following reaction taking place:



The test is carried out as follows: A small amount of the substance is put in a small test-tube, Fig. 23, a few grains of zinc and a little dilute sulphuric acid are added, and a wad of cotton is placed near the top of the tube as a filter. Over the mouth of the tube a piece of filter-paper is placed, with a crystal of silver nitrate on top.

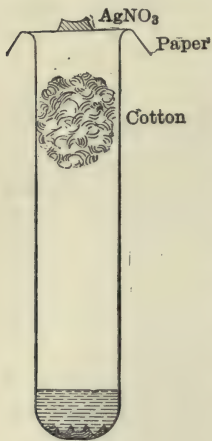
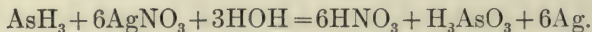


FIG. 23.

If arsenic is present, the silver nitrate is at first turned yellow, but it becomes black very quickly.

This reaction is often used for quickly testing commercial acid for arsenic, but it is not as reliable as the Bettendorff test (page 214), because phosphine\* and stibine give a similar reaction with silver nitrate, while they are not reduced by stannous chloride.

If arsine is allowed to act upon a dilute solution of silver nitrate, the yellow compound  $\text{AsAg}_3 \cdot 3\text{AgNO}_3$  is not formed, for it is immediately decomposed hydrolytically, according to the equation



If the precipitated silver is filtered off, and ammonia then poured on top of the filtrate, the neutral zone will appear yellow owing to the formation of silver arsenite.

This reaction never takes place quite quantitatively; the deposited silver invariably contains a little silver arsenide,  $\text{Ag}_3\text{As}$ .

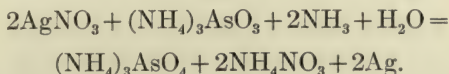
If the silver solution is made ammoniacal, it is true that all the arsine will be absorbed but the deposited silver still contains a little arsenic and the solution a small quantity of ammonium

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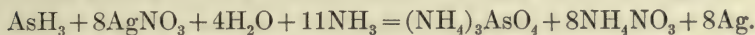
\* Commercial zinc often contains a small quantity of phosphorus.



arsenate. If, however, the solution containing the silver nitrate and ammonium arsenite is heated to boiling, then the arsenite is oxidized quantitatively to arsenate with deposition of silver:\*

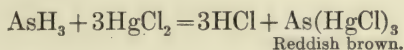


Under these conditions eight atoms of silver are deposited for each molecule of arsine:



If the deposited silver is filtered off and the filtrate carefully neutralized with nitric acid, a brown precipitate of silver arsenate is formed.

Somewhat less sensitive than the original Gutzeit test, although very satisfactory, is the modification recommended by Flückiger† and Lehmann.‡ Instead of allowing the arsine to act upon silver nitrate, it is brought into contact with mercuric chloride§ paper, which is turned reddish brown by a little arsine and yellow by considerable arsine:||



These two last arsenic compounds are characterized by their insolubility in 80 per cent. alcohol.

Stibine gives no reaction in the above test when little of it is

\* Cf. Reckleben, Lockemann and Eckardt, *Z. anal. Chem.*, **1907**, 671.

† *Arch. Pharm.* [3], **1889**, 27.

‡ *Pharm. Ztg. Berlin*, **1892**, 36.

§ For preparing the mercuric chloride paper, some filter paper is moistened with an alcoholic solution of mercuric chloride, the alcohol allowed to evaporate, and the process repeated four or five times.

|| August Gottlieb, *J. Soc. Chem. Ind.*, **22**, 191 (1903).

\P Besides the above compounds,  $\text{AsH}_2(\text{HgCl})$  and  $\text{As}_2\text{Hg}_3$  are known. Cf. Partheil, *Arch. Pharm.*, **237**, 121.

present, but the presence of somewhat more of it causes the formation of a brown spot which is soluble in alcohol. If, however, arsenic and antimony are both present, the former is recognized by cutting out the spot from the rest of the filter-paper and placing it in 80 per cent. alcohol, whereby the brown spot due to the antimony is removed in a short time and the yellow arsenic spot appears plainly. When considerable antimony is present, the test fails; a gray-black spot is produced which does not disappear on treatment with alcohol.

3. **The Reinsch Test** is very easy to make, but it is not as sensitive as the tests just mentioned.

If a strip of polished copper foil is added to a solution of arsenious acid, the copper is colored gray owing to the deposition of the arsenic on the copper, forming copper arsenide of the formula  $\text{As}_2\text{Cu}_5$ .

From concentrated solutions the arsenic separates out in the cold, but from dilute solutions only on warming. If considerable arsenic is present, the gray copper arsenide drops off from the copper. Antimony is also precipitated on copper from its solutions, so that the deposit must be tested for arsenic in the dry way. Arsenic acid is also reduced by copper, but only on warming.

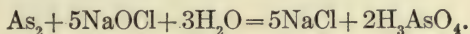
The Reinsch test is often used in testing wall-papers for arsenic. The pieces of paper are treated with a little hydrochloric acid (1:2), a piece of copper foil added, and warmed. A gray deposit on the copper indicates the presence of arsenic.

To confirm this test, the piece of gray copper foil is placed in a tube of difficultly fusible glass and heated in a stream of hydrogen gas; an arsenic mirror is produced which can be tested as described on page 223.

## REACTIONS IN THE DRY WAY.

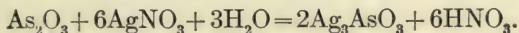
Metallic arsenic burns, giving off a garlic odor. Mixed with sodium carbonate and heated on charcoal, all arsenic compounds give this odor.

Oxygen compounds of arsenic are easily reduced to metal in the upper reducing flame. On holding a porcelain dish (glazed on the outside), filled with water, directly over the sample, the metallic vapors are condensed on the dish, forming a brownish-black coating which is soluble in sodium hypochlorite solution, disappearing instantly, the arsenic being oxidized to arsenic acid:



If the porcelain dish is not held closely above the reducing flame, but above the upper oxidizing flame, the arsenic vapors are burned with a bluish flame to white arsenious oxide which deposits on the dish.

If this deposit is moistened with silver nitrate, and ammonia vapors blown upon it, a yellow coloration due to  $\text{Ag}_3\text{AsO}_3$  is formed, which disappears if more ammonia is allowed to act upon it (difference from antimony):



The ammonia serves to neutralize the nitric acid formed by the reaction, but the precipitate dissolves in excess of ammonia as well as in nitric acid.

**ANTIMONY, Sb. At. Wt. 120.2.**

Sp. Gr. = 6.7-6.8. M. Pt. = 630° C. B. Pt. = about 1450° C.

*Occurrence.*—Antimony seldom occurs free in nature, although large amounts of the metal have been found recently in Australia. The most important compounds containing antimony are (as with arsenic) the sulphur compounds. Stibnite,  $\text{Sb}_2\text{S}_3$ , orthorhombic, is



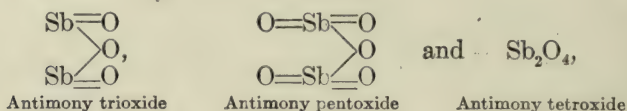
found in Japan in beautiful crystals. The occurrence of kermesite,

$\begin{array}{c} \text{Sb}=\text{S} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{Sb}=\text{S} \end{array}$ , is very interesting, as this compound is often met with in analysis.

Of the oxygen compounds the dimorphous antimony trioxide is known as isometric senarmonite and orthorhombic valentinite. Antimony also occurs in many sulpho salts, of which the tribasic silver sulphoantimonate, or pyrargyrite,  $\text{Sb}(\text{SAg})_3$ , may be mentioned.

Antimony is a silver-white, brittle metal. It burns readily in the air to antimony trioxide. The solvent for antimony is aqua regia, by which it is converted into chloride. Nitric acid attacks antimony, changing it into  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ , which dissolve slightly in concentrated acid, but are insoluble in dilute acid.

Antimony forms three oxides:



of which the latter may be regarded as antimonyl antimonate,

$\begin{array}{c} \text{Sb}=\text{O} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{—O(SbO)} \end{array}$ , and is a very indifferent substance chemically. An-

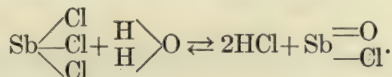
timony trioxide as a rule shows basic properties, while antimony pentoxide has more the character of an acid anhydride.

### A. Compounds of Antimony Trioxide.

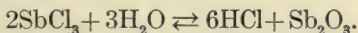
By burning the metal in the air, the trioxide is obtained, which on stronger ignition in the presence of air is changed to the inert  $\text{Sb}_2\text{O}_4$ .

The trioxide is dissolved by concentrated hydrochloric acid, forming antimony trichloride, a compound which (like bismuth chloride) is readily changed into a basic salt by the action of water, the decomposition of which depends upon the "masses" of the

reacting substances. Thus an oxychloride  $\text{Sb} \begin{smallmatrix} \text{=O} \\ \text{---Cl} \end{smallmatrix}$  is known, which is formed according to the following equation:



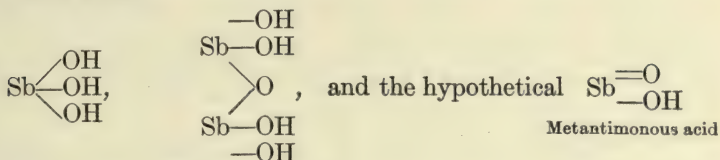
In the presence of a large amount of water some oxide is formed with the oxychloride:



A mixture of oxychloride and oxide is known as "algarot" powder,  $\text{Sb}_2\text{O}_3 \cdot 2\text{SbOCl}$ .

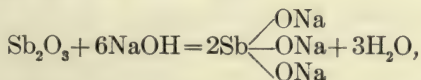
By boiling with considerable water the oxide alone is obtained.

Antimony trioxide forms three hydroxides, which behave as very weak acids:

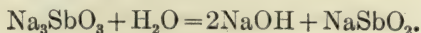


Orthoantimonous acid    Pyroantimonous acid

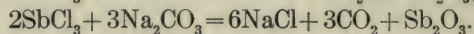
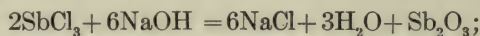
Salts of the metantimonous acid are known, although the free acid itself has never been isolated. On boiling the oxide  $\text{Sb}_2\text{O}_3$  with concentrated caustic soda or potash, it goes into solution, but on dilution with considerable hot water  $\text{Sb}_2\text{O}_3$  separates out again. On filtering this off, tetragonal crystals of  $\text{Sb} \begin{smallmatrix} \text{=O} \\ \text{---ONa} \end{smallmatrix}$  are deposited on cooling; which are, however, very unstable, and are decomposed by standing in the air into sodium carbonate and antimony trioxide. By dissolving antimony trioxide in strong alkali, the orthoantimonate must be formed first:



which is hydrolytically decomposed on dilution into metantimonite and alkali hydroxide:



The latter is decomposed by more water into trioxide and alkali hydroxide; so that on adding to a solution of the trichloride either sodium hydroxide or carbonate, an almost quantitative precipitation of  $\text{Sb}_2\text{O}_3$  will be obtained:

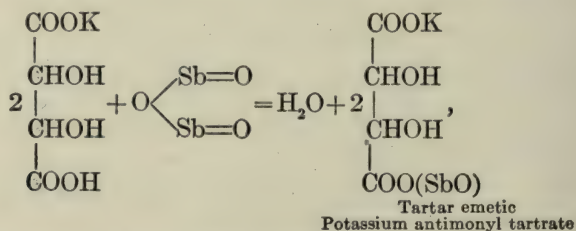


Antimony oxychloride,  $\text{Sb} \begin{smallmatrix} \text{O} \\ \text{---} \\ \text{Cl} \end{smallmatrix}$ , and sodium metantimonite,  $\text{Sb} \begin{smallmatrix} \text{O} \\ \text{---} \\ \text{Na} \end{smallmatrix}$ , contain, as do many other compounds, the univalent group,  $\text{Sb} \begin{smallmatrix} \text{O} \\ \text{---} \end{smallmatrix}$ , which is known as the antimonyl group.

Antimony oxychloride, therefore, can be regarded as antimonyl chloride, and sodium metantimonate as antimonyl oxide of sodium. Antimonyl nitrate,  $\text{Sb} \begin{smallmatrix} \text{O} \\ \text{---} \\ \text{NO}_3 \end{smallmatrix}$ , is also known, and antimonyl sulphate,  $(\text{SbO})_2\text{SO}_4$ . All these compounds are easily hydrolyzed into acid and oxide, so that they are rarely met with in the course of analysis, with the exception of antimonyl chloride.

The antimonyl compounds of certain organic acids (such as tartaric acid) are very much more stable.

On boiling antimony trioxide with a solution of potassium acid tartrate, it goes readily into solution, forming the so-called "tartar emetic,"



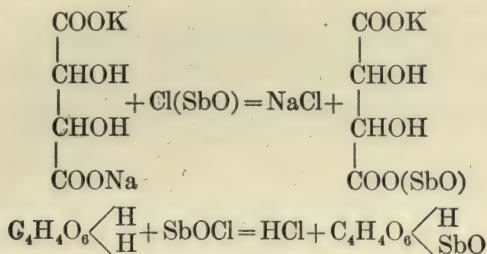
which is comparatively soluble in water.

100 parts of water dissolve at

8.7° C.....	5.26 parts of salt
21° C.....	7.94 " " "
31° C.....	12.20 " " "
50° C.....	18.18 " " "
75° C.....	31.25 " " "



Not only antimonyl oxide,  $\text{Sb}_2\text{O}_3$ , but all antimonyl compounds are soluble in alkali tartrate solution, forming tartar emetic; thus, for example, antimonyl chloride readily dissolves in Rochelle salt, or tartaric acid:

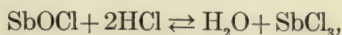


Tartar emetic \* is the most important antimony compound of commerce. Consequently it will be worth while to say a few words with regard to its behavior toward acids.

If an aqueous solution of potassium antimonyl tartrate is treated with hydrochloric acid, a white precipitate of antimonyl chloride is formed,

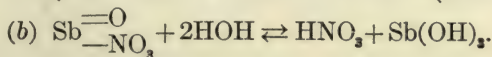
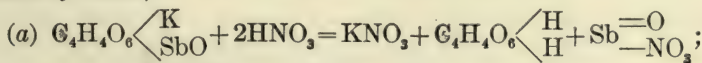


which readily dissolves in more hydrochloric acid,



but by the addition of more water is reprecipitated, etc.

Sulphuric and nitric acids precipitate orthoantimonous acid from a solution of potassium antimonyl tartrate; for the antimonyl compound, which is at first formed, is immediately decomposed by water,



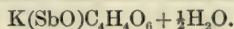
#### REACTIONS OF ANTIMONOUS COMPOUNDS IN THE WET WAY.

1. **Water** precipitates at first a basic salt which is changed into oxide by more water.

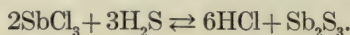
2. **Sodium Hydroxide, Ammonia, and Alkali Carbonates** precipitate amorphous hydrated oxide.

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\* Tartar emetic crystallizes with half a molecule of water:

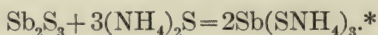


3. **Hydrogen Sulphide** precipitates, from solutions which are not too acid, flocculent, orange-red antimony trisulphide:



As is indicated in the equation, the antimony trisulphide is soluble in hydrochloric acid; in concentrated acid (1 : 1) it is readily soluble (difference from arsenic); so that in order to precipitate antimony by means of hydrogen sulphide, the solution must be quite dilute. In case we have a solution of antimony chloride in hydrochloric acid, we do not attempt to dilute very much at first, for the oxychloride will precipitate out if we do; but we conduct hydrogen sulphide into the solution for some time, then dilute with water, and saturate once more with hydrogen sulphide. If we do not proceed in this way, and attempt to precipitate from a solution which is too acid, the clear filtrate will become turbid as soon as it comes in contact with more water (from a moist beaker, perhaps). In such a case the solution must be largely diluted with water, then filtered again.

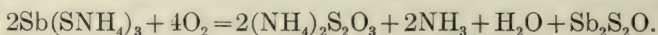
Antimony trisulphide is soluble in ammonium sulphide, forming a sulpho salt:



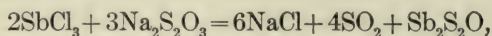
If yellow ammonium sulphide is employed, ammonium salts of sulphoantimonic acid are obtained:



If the solution of ammonium sulphoantimonate is boiled for a long time in the air, the red-colored oxysulphide is often precipitated:



By boiling antimony chloride with sodium thiosulphate, the oxysulphide is also obtained,

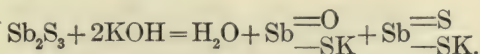


which, on being warmed with ammonium sulphide, redissolves, forming the sulpho salt.

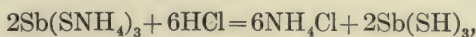
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\* The triammonium salt has never been isolated, the mono salt,  $\text{Sb} \begin{smallmatrix} \text{=S} \\ \text{---SNH}_4 \end{smallmatrix}$ , alone being known in the solid state. In solution, however, particularly in the presence of considerable ammonium sulphide, the ion  $\text{SbS}_4$  must be present.

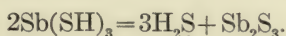
Antimony trisulphide is also soluble in caustic alkali, forming sulpho and oxysulpho salts:\*



These sulpho salts are decomposed by acids, precipitating antimony trisulphide, with evolution of hydrogen sulphide,



and the unstable sulpho acid is further decomposed:



The solution of the sulphide in caustic potash is also precipitated by the addition of acid:



4. **Zinc** precipitates from solutions of antimony compounds metallic antimony. If a piece of platinum foil and a little zinc are placed in an antimony solution containing hydrochloric acid, so that the two metals touch one another, the antimony is deposited on the platinum in the form of a black stain which does not disappear on removal of the zinc (difference from tin).

5. **Potassium Iodide** does not set free iodine when treated with an antimonous solution (difference from antimonie compounds).

## B. Antimonic Compounds.

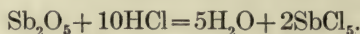
Antimony pentoxide,  $\text{Sb}_2\text{O}_5$ , is formed as a yellow powder by the oxidation of antimony by means of concentrated nitric acid and gently igniting the reaction product (antimonic acid). On strong ignition it loses oxygen and goes over into the very stable antimonyl antimonate  $\text{Sb}_2\text{O}_4$ .

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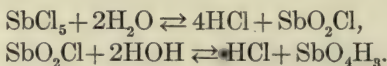
\* It is frequently stated that a mixture of sulpho and oxysalts is formed by the solution of  $\text{Sb}_2\text{S}_3$  in caustic potash. This can hardly be right, because the antimonites of the alkalies are readily decomposed by water into caustic potash and hydrated oxide, the latter separating out. The above solution can be diluted largely without becoming turbid; so it can contain no antimonite.



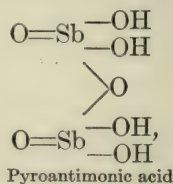
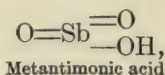
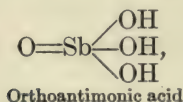
The pentoxide dissolves in concentrated hydrochloric acid, forming the pentachloride



If this solution is treated with water, a white precipitate of antimonious oxychloride,  $\text{SbO}_2\text{Cl}$ , is formed, which, by the addition of more water, is changed on warming into antimonious acid:



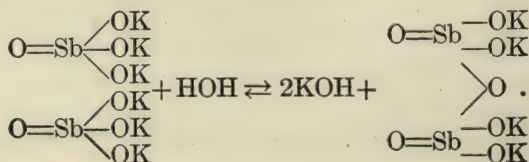
Tartaric acid prevents the precipitation of the oxychloride, as with  $\text{SbOCl}$  (p. 235). Antimony pentoxide is an acid anhydride, and, like the corresponding  $\text{P}_2\text{O}_5$ , can be referred to three acids,



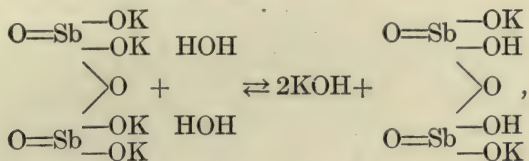
which have all been isolated. The salts of the metantimonious and pyroantimonious acids are the most common. The trimetallic salts of the ortho acid are unknown, but the monometallic salts are known to exist. All antimonates, being salts of a weak acid, are very unstable, being easily hydrolyzed by water.

If antimony pentoxide is fused with an excess of caustic potash, the product of the fusion must contain the trimetallic salt of orthoantimonious acid. If, however, the melt is dissolved in a little water and allowed to crystallize, deliquescent crystals of potassium pyroantimonate,  $\text{K}_4\text{Sb}_2\text{O}_7$ , are formed.

The ortho salt, which is at first formed, is decomposed by water as follows:

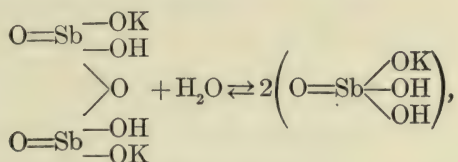


By the action of considerable cold water (or more quickly by rapid boiling with less water) this deliquescent salt is gradually changed into the acid salt, losing KOH,

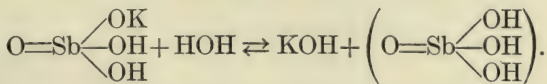


which is a granular powder, difficultly soluble in cold water.\* It dissolves to a considerable extent in water at about 40°–50° C.; this salt is used in testing for sodium, as the sodium salt is very much more insoluble in water.

On boiling the granular potassium salt for a long time with considerable water, it gradually takes on water, forming the easily soluble monometallic salt of orthoantimonic acid,



which is obtained, on evaporating the solution, as a gummy mass of the composition  $2\text{KH}_2\text{SbO}_4 + \text{H}_2\text{O}$ , but on boiling the aqueous solution for a long time, more KOH is lost, with the formation of amorphous orthoantimonic acid:



All antimonates are decomposed by acids, amorphous antimonie acid separating out.

The gummy, monometallic salts give an amorphous precipitation with sodium salts, gradually becoming crystalline, while the potassium pyroantimonate gives a crystalline precipitate immediately.

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\* The granular powder has the composition  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ .

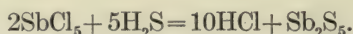
This sensitive reagent for sodium is prepared as follows:

Commercial potassium antimonate (which usually contains considerable antimonite as impurity) is treated with concentrated nitric acid and boiled until no more red fumes are given off; the acid is decanted, and the undissolved, heavy, powdery antimonie acid is washed by decantation with water and then boiled several minutes with a quite concentrated solution of caustic potash. In this way a pure, granular acid potassium salt is obtained. The liquid is cooled, the alkali poured off, 5 or 6 c.c. of water added, quickly heated to boiling, cooled, and filtered. The filtrate thus obtained reacts immediately with a normal solution of a sodium salt.

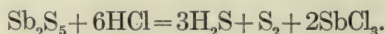
#### REACTIONS OF ANTIMONIC COMPOUNDS IN THE WET WAY.

A solution of the purified potassium antimonate in hydrochloric acid may be used for these reactions.

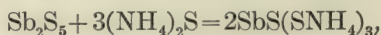
1. **Hydrogen Sulphide** precipitates from fairly acid solutions the orange-red pentasulphide



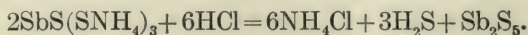
Antimony pentasulphide is soluble in strong hydrochloric acid, forming antimony trichloride, with deposition of sulphur and evolution of hydrogen sulphide:



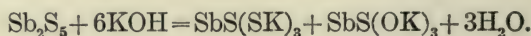
It also dissolves (like the trisulphide) in alkali sulphides, and in alkalies, but not in ammonium carbonate. By treatment with an alkali sulphide, a sulpho salt is obtained,



which is decomposed by the addition of acids, forming the insoluble pentasulphide with evolution of hydrogen sulphide:



Alkalies dissolve the pentasulphide, forming sulpho and oxy-sulpho salts:

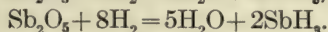
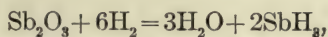




2. **Hydriodic Acid** reduces antimonie compounds in acid solutions, with separation of iodine (difference from antimonous compounds):



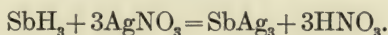
3. **Nascent Hydrogen**.—By treating any solution which contains antimony with nascent hydrogen, stibine is formed:



If the stibine is generated in a Marsh apparatus (cf. p. 222), and the gas is conducted through a red-hot glass tube, a mirror of metallic antimony will be deposited, as with arsenic. But as stibine is much more unstable than arsine, and the antimony itself is much less volatile, the mirror is found nearer the heated place than is the case with arsenic—sometimes before the hottest part of the tube is reached—as the decomposition of the stibine takes place at a much lower temperature than with arsine.

If the stibine is allowed to escape from the tube with the hydrogen, it burns with a pale greenish-white flame to water and antimony trioxide. If a piece of glazed porcelain is held directly over the flame, a deposition of metallic antimony is obtained which is unaffected by a solution of sodium hypochlorite (difference from arsenic).

If stibine is allowed to act upon a solution of silver nitrate,\* a black precipitation of silver antimonide is thrown down:



#### REACTIONS OF ANTIMONY IN THE DRY WAY.

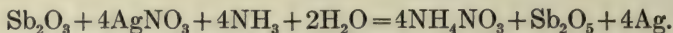
Antimony compounds impart to the flame a pale greenish-white color. Heated with sodium carbonate on charcoal, a brittle metallic button is obtained, surrounded by a white incrustation.

Compounds containing oxygen are reduced in the upper reducing flame to metal, which is volatile and burns in the upper oxidizing flame to trioxide; the latter can be deposited on a glazed porcelain surface. If the deposit is moistened with silver nitrate solution,

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\* Solid silver nitrate is turned yellow at first, then black; exactly the same as by arsine (cf. p. 228).

and ammonia blown upon it, it becomes black, owing to the separation of metallic silver:



**TIN, Sn.** At. Wt. 119.0.

Sp. Gr. = 7.29. M. Pt. = 232° C. B. Pt. = about 1500° C.

*Occurrence.*—Tin does not occur free in nature, but mostly in the form of the dioxide  $\text{SnO}_2$ ,\* as tetragonal tinstone, or cassiterite, isomorphous with rutile ( $\text{TiO}_2$ ), zircon ( $\text{SiO}_2, \text{ZrO}_2$ ), and polianite ( $\text{MnO}_2$ ).

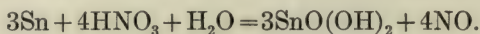
Tin is a silver-white metal, which is ductile and malleable at ordinary temperatures, but at low temperatures and near the melting-point it is so brittle that it can be powdered. In order to pulverize tin, it should be heated in a porcelain dish till it melts; the flame is then removed and the substance is quickly crushed with a pestle. It soon cools to about 200°, becomes brittle and yields a fine powder.

Tin is soluble in hot concentrated hydrochloric acid with evolution of hydrogen:



In the presence of platinum the solution takes place more quickly and at a lower temperature. Dilute hydrochloric acid dissolves tin, but very slowly.

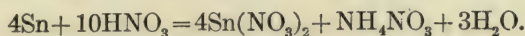
Nitric acid, of sp.gr. 1.2 to 1.3, does not dissolve tin, but oxidizes it to metastannic acid:



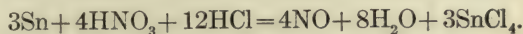
Cold dilute nitric acid dissolves the metal very slowly, without any evolution of gas, forming ammonium and stannous nitrates.

In this reaction the tin is given two positive charges and the nitrogen of nitric acid is reduced from a positive valence of five (toward oxygen) to a negative valence of three (toward hydrogen) thereby losing eight charges. Thus one molecule of nitric acid oxidizes four atoms of tin and eight more molecules of nitric acid are

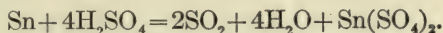
required to form stannous nitrate and one to form ammonium nitrate. Thus the whole reaction may be expressed as follows:



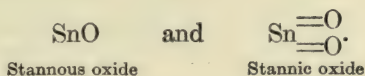
Aqua regia dissolves tin, forming stannic chloride:



Tin dissolves in dilute sulphuric acid very slowly, but readily in hot concentrated acid, forming stannic sulphate, with evolution of sulphur dioxide:



Tin forms two oxides:

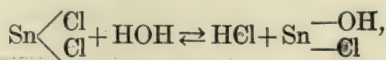


Salts are known corresponding to both these oxides—stannous and stannic salts. The former contain bivalent tin and the latter quadrivalent tin.

### Stannous Compounds.

Stannous oxide (according to the way it is prepared) is either an olive-green or a black powder, which, on being warmed in the air, like all stannous compounds readily changes to stannic oxide. By dissolving stannous oxide (or, better still, the metal itself) in hydrochloric acid, stannous chloride is obtained, which is the most important of all the stannous salts. This salt, with two molecules of water of crystallization,  $\text{SnCl}_2 + 2\text{H}_2\text{O}$ , is the so-called "tin salt" of commerce.

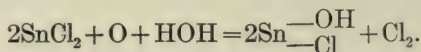
Fresh crystals of "tin salt" will dissolve clear in a little water; if more water is added the solution becomes turbid, owing to the formation of a basic salt,



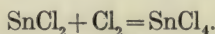
which is readily soluble in hydrochloric acid.



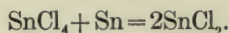
The clear concentrated solution also becomes turbid on standing in the air, owing to the formation of the same basic salt with loss of chlorine:



The chlorine, however, is not set free, but unites with some of the unchanged stannous chloride, forming stannic chloride:



If tin tetrachloride is treated with metallic tin, the latter goes into solution and the former is reduced to stannous chloride:



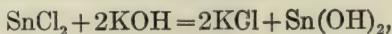
Consequently, in order to *maintain* a solution of stannous chloride, hydrochloric acid should be added to prevent the formation of the basic salt, and metallic tin to keep the solution in the stannous condition.

Such a solution constantly grows more concentrated, owing to the gradual solution of the tin. In order to keep a solution of stannous chloride at a definite concentration (only necessary for purposes of quantitative analysis) the hydrochloric acid solution is kept away from air in an atmosphere of carbon dioxide without the addition of metallic tin.

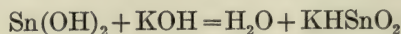
Nearly all stannous compounds are colorless; the oxide (as already mentioned) is black and the sulphide dark brown.

#### REACTIONS IN THE WET WAY.

1. **Potassium and Sodium Hydroxides** produce a white precipitate of gelatinous stannous hydroxide,



which is readily soluble in an excess of the precipitant, forming potassium stannite\*:




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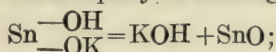
\* According to Hantzsch the solution contains:



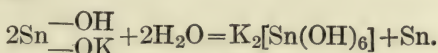
The hydroxide is also readily soluble in hydrochloric acid. Stannous hydroxide, therefore, behaves partly as an acid and partly as a base (like the hydroxides of zinc, aluminium, and chromium).

The alkaline solution of an alkali stannate is often changed brownish black or black (particularly on warming, or when very concentrated caustic alkali is used), owing to the separation of either metallic tin or stannous oxide:

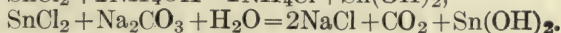
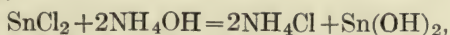
From dilute potassium hydroxide solutions there gradually separates on standing, or more rapidly on heating, the black monoxide,



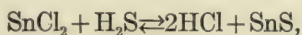
and from quite concentrated alkali the precipitate is almost wholly black metallic tin:



**2. Ammonia and Alkali Carbonates** precipitate the white hydroxide, which is not absolutely insoluble in an excess of the precipitant:

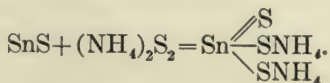


**3. Hydrogen Sulphide** produces (in solutions which are not too acid) a brown precipitate of stannous sulphide,

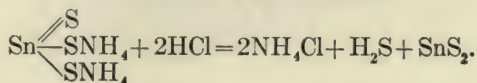


readily soluble in strong hydrochloric acid; therefore no stannous sulphide is precipitated if the solution is very acid. After diluting a strongly acid solution with water, however, stannous sulphide is completely precipitated on saturating the solution with hydrogen sulphide gas.

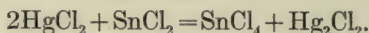
Stannous sulphide is insoluble in ammonia and ammonium carbonate (difference from arsenic); also in colorless ammonium sulphide (difference from arsenic and antimony); but is readily soluble in yellow ammonium sulphide, forming ammonium sulphostannate:



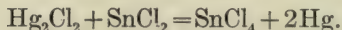
If the solution of ammonium sulphostannate is acidified with any acid, yellow stannic sulphide is precipitated:



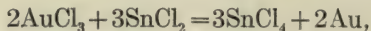
4. **Mercuric Chloride** produces in solutions of stannous salts a white precipitate of mercurous chloride:



But if the stannous chloride is present in excess, the mercurous chloride will be further reduced to gray mercury:

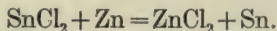


5. The **Gold Test** is much more sensitive. If to a solution of chloride of gold a solution containing a trace of stannous chloride is added, finely divided metallic gold will be precipitated,



which appears brown by transmitted light, and bluish-green by reflected light.

6. **Metallic Zinc** precipitates tin from both stannous and stannic solutions as a spongy mass, which adheres to the zinc:



The finely-divided, spongy metal is easily soluble in strong hydrochloric acid; the experiment must not, therefore, be made in strongly acid solutions, as the tin is loosened from the zinc by the violent evolution of hydrogen and is redissolved by the acid. The test is best made by adding a drop of the (not too acid) solution to a piece of platinum foil, and then placing a piece of bright zinc so that it comes in contact with both the solution and the platinum. The tin is precipitated partly on the zinc and partly on the platinum,\* in the form of a gray stain, which disappears from the latter as soon as the zinc is removed, provided the solution is still acid (difference from antimony). If the zinc is kept in contact with the acid until the evolution of hydrogen ceases, the tin stain will not disappear from the platinum, because all the acid has been used up. On adding a few drops of concentrated hydrochloric acid to the

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\* In weakly acid solutions tin is precipitated chiefly on the zinc; in strongly acid solutions, chiefly on the platinum.



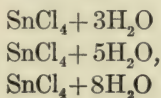
platinum, the stain quickly disappears with an evolution of hydrogen. The reason why the tin is deposited on the platinum notwithstanding the presence of acid is that a galvanic current is formed by the contact of the zinc with the platinum, which flows from the zinc to the platinum; the platinum thus serves as a cathode, and the zinc is deposited upon it. On removing the zinc the current stops and the stain disappears.

### Stannic Compounds.

The stannic compounds (which are all colorless, with the exception of the yellow sulphide  $\text{SnS}_2$ ) cannot be obtained by the solution of the oxide  $\text{SnO}_2$ , from which they are derived, because the oxide is attacked with difficulty by acids. They are obtained indirectly from metallic tin or from stannous compounds.

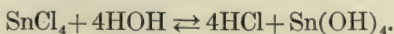
The simple stannic compounds are all, more or less readily, completely hydrolyzed by water, so that the analyst almost never meets with them. The nitrate  $\text{Sn}(\text{NO}_3)_4$  and the sulphate  $\text{Sn}(\text{SO}_4)_2$  are quickly decomposed, in the cold, into acid and stannic hydroxide. The halogen compounds are much more stable, and are decomposed only by boiling with considerable water. For the following reactions, therefore, we will assume that we have a solution of stannic chloride to work with.

Stannic chloride is a colorless liquid, which fumes in the air and boils at  $120^\circ \text{C}$ . On adding a little water it solidifies, forming crystals of monoclinic hydrates,



of which the salt with  $5\text{H}_2\text{O}$  is used commercially as a mordant in dyeing.

On adding more water to these hydrates they dissolve, forming a clear solution, which on boiling (the freshly-prepared dilute solution) gradually becomes turbid, owing to the precipitation of voluminous stannic hydroxide:

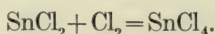


If the solution is very dilute it becomes turbid in the cold. The stannic acid thus formed is not precipitated quantitatively, either

in the cold or on boiling, because a considerable amount remains in the hydrosol form. By "salting out" the hot solution (best with ammonium nitrate), the stannic acid may be completely precipitated.

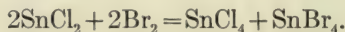
A solution of stannic chloride can be most readily obtained for analytical purposes by chlorinating or brominating a solution of stannous chloride.

On adding chlorine to a solution of stannous chloride, stannic chloride is formed in the cold:



As, however, chlorine is colorless in a dilute solution, it is difficult to tell when the oxidation is complete; it is more easily ascertained if bromine is used.

On adding strong bromine water, drop by drop with constant stirring, to a solution of stannous chloride, the brown color will disappear as long as any stannous chloride remains unchanged, and the solution becomes colored by the bromine only when the oxidation is complete. The solution then contains a mixture of stannic chloride and stannic bromide:



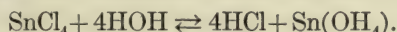
Just as platinum tetrachloride combines with hydrochloric acid to form chloroplatinic acid, so tin tetrachloride unites with hydrochloric acid, forming chlorostannic acid,



and yields, like the former, beautifully crystalline, easily soluble salts with the alkalis, of which the ammonium salt  $(\text{NH}_4)_2[\text{SnCl}_6]$  is an article of commerce being known as "pink salt." The above-mentioned stannic chloride,  $\text{SnCl}_4$ , is sometimes designated as  $\alpha$ -stannic chloride, to distinguish it from a compound (which we shall soon study) known as  $\beta$ -stannic chloride (stannyl chloride).

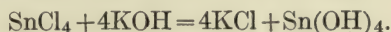
### Reactions of the $\alpha$ -Stannic Compounds.

1. **Hydrochloric and Sulphuric Acids** produce in moderately concentrated solutions of stannic chloride no precipitation, even on long standing (difference from  $\beta$ -stannic compounds). In very dilute sulphuric acid solutions a precipitate of basic sulphate is sometimes obtained. In very dilute hydrochloric acid solutions, also, a slight turbidity is often formed, which increases on boiling the solution:



2. **Potassium and Sodium Sulphates** produce no precipitation in the cold (difference from stannyl chloride), but on boiling all the tin is precipitated as hydroxide.

3. **Potassium or Sodium Hydroxide.**—On adding caustic alkali to a solution of a stannic salt, a voluminous, gelatinous, white precipitate is obtained:



The precipitate has the above formula when dried in the air, and the formula  $\text{SnO}(\text{OH})_2$  if dried over sulphuric acid.

The precipitate dissolves readily in an excess of alkali hydroxide, forming salts which are not derived from either of the above compounds, but from  $\text{H}_2 \cdot [\text{Sn}(\text{OH})_6]$ , which has itself never been isolated:



The hydroxide dissolves in ammonia also, but only in the absence of ammonium salts.

By dissolving in alkali, stannic hydroxide behaves as an acid, and according to Bellucci and Parravano,\* the hexahydroxystannic acid stands in the same relation to chlorostannic acid as hexahydroxyplatinic acid to chloroplatinic acid:



The salts of hexahydroxystannic acid are designated briefly as stannates, or  $\alpha$ -stannates, to distinguish them from the  $\beta$ -stannates or metastannates, which are derived from the polymer  $(\text{H}_2\text{SnO}_3)_5$  (see p. 251).

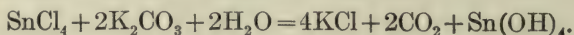
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\* Z. anorg. Chem., 45 (1905), p. 156.



The ready solubility of  $\alpha$ -stannic acid in cold dilute mineral acids is very characteristic. It dissolves promptly in hydrochloric, nitric, and sulphuric acids, behaving, in this respect, as a base. By boiling the dilute acid solution (particularly the sulphuric acid solution) stannic acid is reprecipitated, which is soluble in cold dilute acids provided the boiling has not been continued too long. In the latter case the  $\beta$ -stannic acid is formed, which is insoluble in dilute acids.

4. **Potassium Carbonate** precipitates stannic acid from stannic chloride solutions, which is completely soluble in an excess of the reagent (difference from  $\beta$ -stannic acid):



5. **Sodium Carbonate** behaves similarly, but the precipitate is not so easily soluble in an excess.

6. **Ammonia** precipitates stannic acid from a solution of stannic chloride; tartaric acid prevents the precipitation (difference from  $\beta$ -stannic acid).

### Reactions of the $\beta$ -Stannic Compounds.

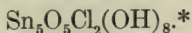
(*Metastannates.*)

By the oxidation of metallic tin with hot nitric acid of sp. gr. 1.3 stannic nitrate is first formed, which, by boiling with water, is completely hydrolyzed, forming nitric acid and metastannic acid.

Metastannic acid is a white powder insoluble in nitric acid, and when dried over sulphuric acid has the formula  $\text{H}_2\text{SnO}_3$ . This is of the same empirical composition as the hydroxide precipitated by treating a stannic chloride solution with alkalies, though differing essentially from it in many reactions.

While the  $\alpha$ -stannic acid (as already mentioned) is easily soluble in dilute mineral acids, the  $\beta$ -stannic acid is almost insoluble therein.

1. If the  $\beta$ -stannic acid is treated for a short time with concentrated hydrochloric acid, a chloride is formed which is insoluble in hydrochloric acid, but readily soluble in water. The solution contains the so-called  $\beta$ -stannic chloride (though the designation stannyl chloride would be more suitable) of the composition,




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\* R. Engel, Chem. Ztg., 1897, pp. 309 and 859.

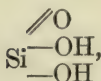
2. On treating the aqueous solution of stannyl chloride with hydrochloric acid, almost all the tin is reprecipitated in the form of a highly chlorinated compound of the composition:



3. If an aqueous solution of stannyl chloride is heated to boiling, almost all the tin is precipitated as  $\beta$ -stannic acid, which is insoluble in dilute acids.

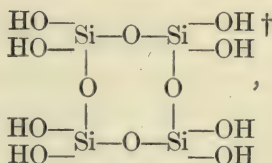
This differing behavior of the two acids, as well as of the two chlorides, can be explained as follows: Silicic acid, which is closely related to stannic acid, exists in innumerable silicates in different polymeric forms; as, for example, in the cases of the minerals of the pyroxene and amphibole groups,

Wollastonite,  $\text{CaSiO}_3$ ,  
is a derivative of ordinary  
metasilicic acid,

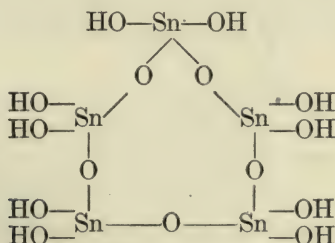


and

Tremolite,  $\text{CaMg}_3\text{Si}_4\text{O}_{12}$ ,  
is a derivative of the poly-  
meric silicic acid,



and it is highly probable that the stannic acid can exist in analogous polymers. One of these polymers seems to possess the composition  $[\text{SnO}_3\text{H}_2]_5$ , to which we can ascribe the following structural formula:



If such a compound is treated with hydrochloric acid, the hydroxyl groups will, first, be replaced by chlorine, and a compound

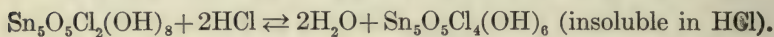
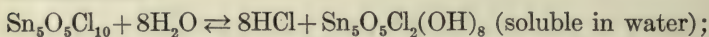
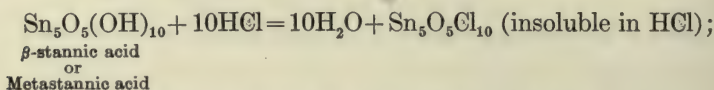
\* Weber, Jahresber., 1869, 244, and Pogg. Ann., 122, 358.

† Groth, Tabellarische Uebersicht d. Min. 1893, p. 148.

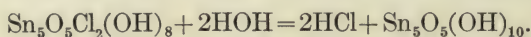
will be obtained containing tin, oxygen, and chlorine, e.g.,  $\text{Sn}_5\text{O}_5\text{Cl}_{10}$ .

This hypothetical compound of the  $\beta$ -stannic acid is hydrolyzed, forming different chlorides of varying solubilities. Thus R. Engel found that the chloride  $\text{Sn}_5\text{O}_5\text{Cl}_2(\text{OH})_8$  is soluble in water; and Weber showed that from an aqueous solution of the latter, hydrochloric acid precipitates the compound  $\text{Sn}_5\text{O}_5\text{Cl}_4(\text{OH})_6 + 4\text{H}_2\text{O}$ .

The reaction which takes place on dissolving the  $\beta$ -stannic acid in hydrochloric acid and water may be satisfactorily expressed by the following equations:



On boiling the aqueous solution, complete hydrolysis takes place:



If the  $\beta$ -stannic acid is treated for a long time with concentrated hydrochloric acid, the ring  $\text{Sn}_5\text{O}_5$  is finally broken down, so that the tin goes into solution in the form of ordinary  $\alpha$ -stannic chloride:

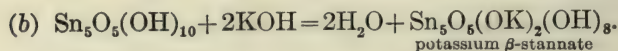
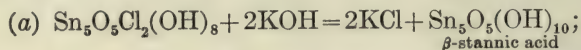


Further reactions of stannyl chloride ( $\beta$ -stannic chloride) are:

4. **Sulphuric Acid** precipitates from solutions of stannyl chloride white stannyl sulphate, which on being washed with water is completely changed to  $\beta$ -stannic acid (difference from  $\alpha$ -stannic chloride).

5. **Potassium and Sodium Sulphates** cause the same reaction as sulphuric acid.

6. **Potassium Hydroxide** throws down in solutions of stannyl chloride a voluminous precipitate of  $\beta$ -stannic acid, which does not dissolve in an excess of the concentrated precipitant, but forms a  $\beta$ -stannate easily soluble in water and dilute caustic potash:



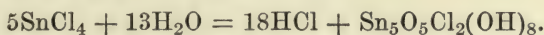


By long treatment of the potassium  $\beta$ -stannate with concentrated caustic potash, it gradually goes into solution, forming  $\alpha$ -potassium stannate. This change takes place more readily by fusing  $\beta$ -stannic acid with solid potassium hydroxide in a silver crucible.

If a dilute solution of a mineral acid is added to the  $\beta$ -potassium stannate, a voluminous precipitate is formed, consisting partly of  $\beta$ -stannic acid (insoluble in an excess of mineral acids) and partly of  $\alpha$ -stannic acid (readily soluble in an excess of the acid). The latter compound is formed when a very concentrated solution of caustic potash was used in forming the potassium salt.

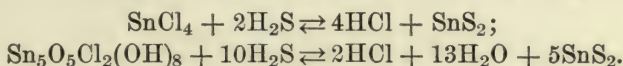
7. **Ammonia** also precipitates  $\beta$ -stannic acid, even in the presence of tartaric acid (difference from  $\alpha$ -stannic chloride).

As we have seen, the  $\alpha$ -compounds may be readily changed into  $\beta$ -compounds and conversely. *The dilute aqueous solutions of the  $\alpha$ -compounds are gradually changed, at the ordinary temperature, into  $\beta$ -compounds, but more quickly on boiling; thus stannic chloride changes to stannyl chloride:*



*The  $\beta$ -compounds are changed into  $\alpha$ -compounds by boiling with concentrated hydrochloric acid or concentrated caustic potash.*

8. **Hydrogen Sulphide** precipitates (from not too acid solutions) yellow stannic sulphide from both the  $\alpha$ - and the  $\beta$ -compounds:\*

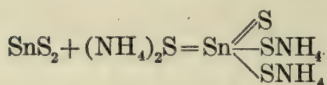


Stannic sulphide is soluble in hydrochloric acid; hydrogen sulphide will cause no precipitation, therefore, if the solution is very acid. If such a solution, saturated with hydrogen sulphide, is largely diluted, the sulphide will precipitate out.

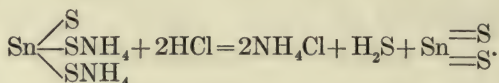
The yellow sulphide is the sulpho-anhydride of the sulpho acid; it dissolves, therefore, in alkali sulphide, forming salts soluble in water:

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\* From  $\beta$ -stannic solutions hydrogen sulphide produces a precipitate, but very slowly, the  $\text{SnS}_2$  remaining largely in the hydrosol form. By the addition of salts it is coagulated, and separates out in a flocculent form, usually mixed with  $\beta$ -stannic acid (cf. Z. anorg. Chem. 28, 140). If the stannyl chloride solution is heated on the water-bath in a pressure flask, the tin is quickly precipitated as greenish-yellow sulphide.



Acids precipitate from such a solution the yellow stannic sulphide



The sulphide is insoluble in ammonia and ammonium carbonate (difference from arsenic). By means of concentrated nitric acid it is easily oxidized to  $\beta$ -stannic acid; or by roasting in the air it can be completely changed to tin dioxide.

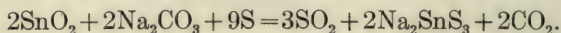
The sulphide obtained in the dry way, known as "mosaic gold," is not attacked by nitric acid, and is also insoluble in alkali sulphides. It dissolves on treatment with aqua regia, forming stannic chloride with separation of sulphur. It is most readily brought into solution by fusing with sodium carbonate and sulphur (see below).

9. **Mercuric Chloride** produces no precipitation in solutions of stannic salts.

Tin dioxide as it occurs in nature, and the artificially produced oxide, after strong ignition, are both insoluble in all acids. They can be brought into solution by the following methods:

1. Fusion with sodium carbonate and sulphur;
2. " " caustic potash or soda;
3. " " potassium cyanide;
4. Reduction of hydrogen at a high heat.

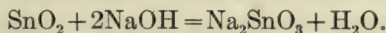
(1) *Fusion with Sodium Carbonate and Sulphur.*—The dry substance is placed in a small porcelain crucible, mixed with six times as much calcined sodium carbonate and sulphur (equal parts mixed together), covered, and heated over a small flame until the excess of sulphur has distilled off and burned. This operation requires about twenty minutes. The crucible is then allowed to cool, its contents are treated with warm water, and the solution filtered if necessary:



If iron, lead, copper, or any other metal forming sulphides insoluble in water and ammonium polysulphide are present, these

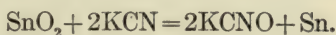
remain undissolved as sulphides, and are separated from the tin by filtration.

(2) *Fusion with Sodium Hydroxide.*—The sodium hydroxide is melted in a silver crucible, which is placed within a porcelain crucible to protect the silver from the injurious action of the gas flame, until all water has been driven off (the fusion becoming quiet) and allowed to cool somewhat; the finely-powdered, dry substance is added, and the mixture is again heated until the fusion is clear. After cooling, the product is dissolved in water:



Stannic oxide is not completely attacked by fusion with sodium or potassium carbonate.

(3) *Fusion with Potassium Cyanide.*—Some potassium cyanide is melted in a porcelain crucible, the powdered stannic oxide is added, and the mixture is fused until the separated tin has melted together:



After cooling, the mass is treated with water, the tin filtered off, flattened into foil, and then dissolved in concentrated hydrochloric acid.

(4) *Reduction in a Stream of Hydrogen.*—The substance is put in a platinum boat and the latter is placed in a glass tube, open at both ends, which is made of difficultly-fusible glass; hydrogen is conducted into the tube in the cold until the air has been driven out, when it is heated (at a faint-red heat) until no more water is formed:



The metal is then dissolved in hydrochloric acid.

#### REACTIONS IN THE DRY WAY.

If a tin salt is heated with soda (or potassium cyanide) on charcoal, usually only a small malleable button is obtained, which, on taking away the flame, is immediately covered with a white coating of oxide. This can be observed when the flame is allowed to play upon the fusion. If the product is crushed in an agate mortar, a small flake of metallic tin is obtained, which can be distinguished from silver and lead by its insolubility in nitric acid, and by its solubility in hydrochloric acid. This reaction is particularly suitable



for the charcoal-stick test. The borax bead which has been colored pale blue by copper becomes a transparent ruby red in the reducing flame if a trace of tin is added. This is a very sensitive reaction.

For the separation of the sulpho-acids from the sulpho-bases see Table VI, page 258.

**GOLD**, Au. At. Wt. 197.2.

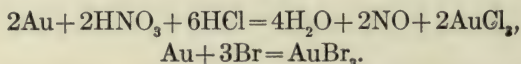
Sp. Gr. = 19.33. M. Pt. = 1063° C.

*Occurrence.*—Gold usually occurs native in quartz and in river sands; also as telluride of gold in sylvanite,  $(\text{AuAg})_2\text{Te}_3$ , and in nagyagite,  $(\text{PbAu})_2(\text{TeSSb})_3$ , and is found in small amounts in many pyrite and other sulphide ores.

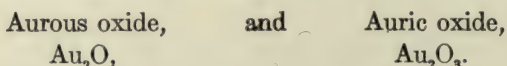
Metallic gold is of a yellow color and melts without being oxidized. It is the most ductile of all metals, and may be hammered into exceedingly thin leaves, which are transparent, with a bluish-green color.

Commercial gold is usually alloyed with copper, silver, or with both metals. Pure gold is designated as 24-carat gold or  $1000/1000$  fine. Fourteen-carat gold contains 14 parts of gold to 10 parts of other metal and 18-carat gold contains 18 parts of gold in 24 parts of the alloy; the former, therefore, contains  $503/1000$  and the latter  $750/1000$  of pure gold.

The proper solvent for gold is aqua regia, but it is also soluble in bromine and chlorine water, forming a trihalogen compound:

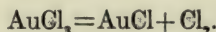


Gold is not attacked by mineral acids. It forms two oxides:



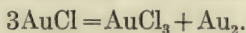
Both of these are exceedingly unstable; on gentle ignition they lose oxygen and are changed to metal (a property common to all "noble" metals).

All gold salts are unstable; even the most stable salt of all, the chloride,  $\text{AuCl}_3$ , is changed by gentle ignition into yellowish-white aurous chloride,  $\text{AuCl}$ :

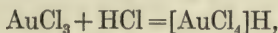


On stronger ignition the last atom of chlorine is lost, and the yellow metal itself is left behind.

Aurous chloride,  $\text{AuCl}$ , is insoluble in water, but on being boiled with water for some time, or very gradually in the cold, it is changed to auric chloride, with deposition of metal:



The solution obtained by dissolving gold in aqua regia always contains auric chloride, so that only the reactions of auric compounds are of interest to the analytical chemist. Auric chloride unites with hydrochloric acid forming chlorauric acid.



which yields beautifully crystalline salts.

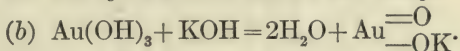
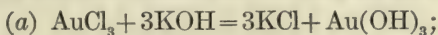
Gold chloride is soluble in ether and can be extracted from its aqueous solutions by means of this solvent.

Auric salts are mostly yellow and readily soluble in water. The sulphide is black and soluble only in aqua regia.

#### REACTIONS IN THE WET WAY.

A solution of chlorauric acid,  $\text{H}[\text{AuCl}_4]$ , should be used for these reactions.

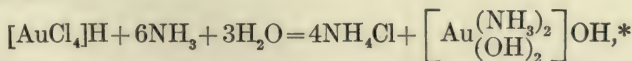
1. **Potassium or Sodium Hydroxide.**—If caustic alkali is cautiously added to a concentrated gold solution, a reddish-brown, voluminous precipitate of auric hydroxide is obtained, which looks exactly like ferric hydroxide. If more caustic alkali is added, however, the gold hydroxide redissolves, forming alkali aurate:



If the bright-yellow solution of potassium aurate is carefully acidified with nitric acid, a precipitate of reddish-brown auric acid is thrown down, which is soluble in nitric acid, but is reprecipitated, for the most part, by dilution and boiling.

As a rule, potassium hydroxide yields no precipitate in solutions of gold chloride, because the gold solution is usually so dilute that the amount of alkali added is sufficient to form the aurate at once.

2. **Ammonia** throws down a precipitate of dirty-yellow, fulminating gold,



which explodes in a dry condition on warming or by concussion.

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\* The formula of fulminating gold is usually expressed as  $\text{AuNH}_2\text{NH}_2 + 3\text{H}_2\text{O}$ .

TABLE VI. SEPARATION OF ARSENIC, ANTIMONY, AND TIN FROM THE COPPER GROUP, AND FROM ONE ANOTHER.

All the metals of the hydrogen sulphide group are assumed to be present in the form of freshly-precipitated sulphides. The washed precipitate is placed in a porcelain dish, treated with yellow ammonium sulphide,\* warmed gently for a short time (with stirring), and then filtered.

#### RESIDUE may contain

HgS, PbS, Bi<sub>2</sub>S<sub>3</sub>, CuS, CdS, and should be examined according to Table V, page 207.

#### SOLUTION [As<sub>2</sub>(NH<sub>4</sub>)<sub>3</sub>, SbS<sub>3</sub>(NH<sub>4</sub>)<sub>3</sub>, SnS<sub>3</sub>(NH<sub>4</sub>)<sub>2</sub>].

The solution is diluted with considerable water, and hydrochloric acid added until the solution reacts acid with litmus. It is then boiled, the precipitated sulphides allowed to settle, the supernatant liquid decanted off, and the residue filtered and washed.

The arsenic, antimony, and tin sulphides are then analyzed by one of the two following methods:

1. The three sulphides (contaminated with considerable sulphur) are boiled with strong hydrochloric acid (1:1) [until the vapors cease to blacken lead acetate paper] and then filtered.

#### RESIDUE [AsS<sub>2</sub> + S].

This is treated with fuming nitric acid in a covered beaker, boiled until completely dissolved and brown fumes cease to be given off, then evaporated to a small volume, an excess of ammonia and some magnesium chloride or magnesium sulphate solution added and the mixture vigorously stirred. If considerable arsenic is present, a precipitate of white crystalline MgNH<sub>4</sub>AsO<sub>4</sub> + Aq will be formed. If only a small amount of arsenic is present, the precipitate will form only on standing. If no precipitate is formed after twelve hours, no arsenic is present.

#### SOLUTION [SbCl<sub>3</sub> + SnCl<sub>4</sub>].

The solution is concentrated to a small volume, a few drops are placed on some platinum foil, and a piece of bright zinc is put in the liquid, so that it comes in contact with both the solution and the platinum. After a few seconds the zinc is removed, and the platinum is examined to see whether a black stain has formed upon it which is insoluble in hydrochloric acid. Such a stain shows *antimony*.

The zinc is again added to the solution and allowed to remain until the evolution of hydrogen almost entirely ceases, when the solution is carefully washed off with distilled water, keeping the zinc and platinum in contact. The zinc is then removed as completely as possible (any adhering tin being scraped off from the foil), dissolved in a few drops of concentrated hydrochloric acid, placed in a small test-tube, and a drop of mercuric chloride added. A white precipitate, which finally turns gray, shows *tin* to be present.



2. The mixture of arsenic, antimony, and tin sulphides (contaminated with sulphur) is heated with a concentrated solution of ammonium carbonate and filtered:

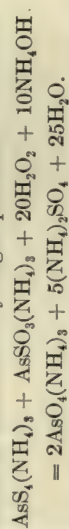
RESIDUE  $[\text{Sb}_2\text{S}_5, \text{SnS}_2, \text{S}]$ .

The sulphides are dissolved in hydrochloric acid and analyzed as above.

SOLUTION  $[\text{AsS}_4(\text{NH}_4)_3 + \text{AsO}_3(\text{NH}_4)_3]$ .

The solution is acidified with hydrochloric acid, which causes yellow arsenic sulphide to be precipitated, showing the presence of *arsenic*. In order to confirm this, the sulphide is dissolved in fuming nitric acid (as above) and the precipitate of magnesium ammonium arsenate is produced.

The transformation of the arsenic sulphide into arsenic acid can be accomplished better by an ammoniacal solution of hydrogen peroxide:



From this solution magnesium chloride precipitates  $\text{MgNH}_4\text{AsO}_4$ .

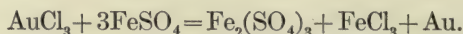
The magnesium precipitate may be tested in the dry way for arsenic by permitting the white incrustation to form on a porcelain dish (see p. 231) and testing this coating with silver nitrate and ammonia.

A yellow deposit shows *arsenic* to be present.

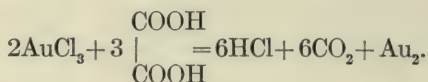
\* Yellow ammonium sulphide is used, because  $\text{SnS}$  is insoluble in colorless ammonium sulphide.

The most important reactions for the detection of gold are those which depend upon the extreme readiness with which the auric compounds are reduced. *Auric compounds are strong oxidizing agents.*

3. **Ferrous Salts** precipitate at ordinary temperatures from neutral or acid solutions all the gold as a brown powder (difference from platinum):

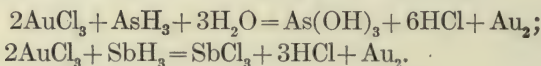


4. **Oxalic Acid** precipitates all of the gold in the cold, but more quickly on warming (difference from platinum):

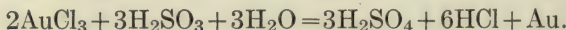


The presence of considerable hydrochloric acid prevents this reaction.

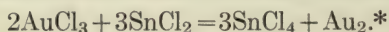
5. **Arsine and Stibine** precipitate gold completely:



6. **Sulphurous Acid** reduces gold solutions:



7. **Stannous Chloride** causes the following reaction to take place:



If the solution tested is strongly acid with hydrochloric acid, the precipitate is pure gold and has the characteristic dark-brown color of the finely-divided metal. In very dilute weakly-acid solutions the so-called Purple of Cassius is thrown down which consists of colloidal gold and tin hydroxide.

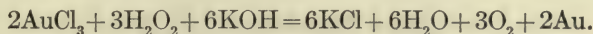
Purple of Cassius is soluble in ammonia and in dilute caustic potash solution, forming reddish liquids. These solutions when cold remain clear for a long time and can even be boiled without decomposition. As the solution is concentrated a flocculent precipitate is formed which will dissolve on the addition of more ammonia.

The brown coloration can be distinctly seen if 0.3 mg. gold are dissolved in 100 c.c. of the solution, and 10 c.c. of the solution are used for the test (=0.03 mg. Au).

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\* Theodor Döring, Chem. Centralbl., 1900, I, p. 735.

8. **Hydrogen Peroxide**\* in alkaline solution immediately precipitates the gold as finely-divided metal:



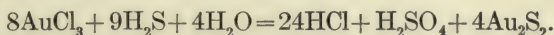
The precipitated metal appears brownish-black by reflected light, but bluish-green by transmitted light;  $\frac{3}{100}$  mg. gold in 10 c. c. of liquid suffice to give a reddish coloration with a bluish shimmer.

9. **Zinc**.—The following gold test is very sensitive.† A few drops of a dilute gold solution are taken; a drop of arsenic acid, two to three drops of ferric chloride, and two to three drops of hydrochloric acid are added; the mixture is then diluted to 100 c. c., and a piece of zinc is dropped in. Around the zinc the solution assumes a purple color, which, by moving the zinc in the solution, is disseminated through it, making it appear pink or purple.

If the solution contains  $\frac{3}{100}$  mg. of gold, within fifteen minutes a beautiful reddish color will be noticed.

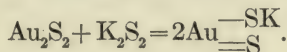
Besides the above reagents many others, such as formaldehyde in the presence of alkali, hydrazine sulphate, etc., are capable of reducing gold from its solutions.

10. **Hydrogen Sulphide** precipitates, in the cold, black gold disulphide from gold solutions:



Gold disulphide is insoluble in acids; but is readily soluble in aqua regia, forming auric chloride,  $\text{AuCl}_3$ .

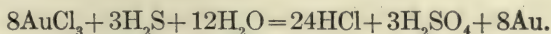
The disulphide is difficultly soluble in ammonium sulphide, but more readily soluble in potassium sulphide, forming a sulpho salt:



From this solution hydrochloric acid precipitates a yellowish-brown sulphide:



From a hot solution hydrogen sulphide precipitates brown, metallic gold:

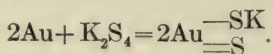


\* Vanino and Seemann, Ber., 1899, 1968.

† Pharm. Chem. Centrabl., 27, 321.



The metallic gold is soluble in hot potassium or sodium polysulphide, forming a sulpho salt:



On account of its softness, gold is always alloyed with silver and copper when used for coins or for jewelry. If such an alloy is treated with nitric acid, the copper and silver are dissolved out, the gold remaining, usually as a brownish powder. The gold is filtered off through a small filter; the filter is dried, rolled together and enveloped in platinum wire; the paper is lighted and allowed to burn quietly. [The ash must not be too strongly heated, for the gold would then melt and alloy with the platinum wire.] The ash is melted with a little soda on a charcoal stick, a gold button forming with the characteristic yellow color. The gold button can be pressed into a leaf in the agate mortar, transferred to a watch-glass, and dissolved in a little aqua regia, forming auric chloride. The solution is carefully evaporated to dryness, the residue dissolved in a little water, and a dilute solution of stannous chloride added, when the presence of gold is shown by the formation of the purple of Cassius. The hydrogen peroxide or zinc tests are still more delicate (see p. 261).

If it is a question of detecting very small amounts of gold (as in the case of many copper coins), the above method is unsuitable. In such a case the gold and silver are extracted by melting them together with lead, and the lead is then separated by oxidation and removal of the lead oxide. The process is as follows: five to ten gm. of the auriferous copper (or more in some cases) are treated with 120 gm. of pure lead in a flat dish of infusible stone (a scorifying-dish), and melted in a muffle, with access of air. The copper and a part of the lead are oxidized, and the oxide unites with the silica of the dish to form a readily fusible slag, which eventually covers the unaffected lead and the dissolved silver and gold. This operation is known as *scorification*. When this point is reached, the molten mass is poured into an iron scorification pan, previously well chalked. As soon as the mass becomes cool, it is removed from the pan, and the slag is hammered off from the enclosed lead button, which is weighed. The button is then placed in a cupel (a sort of crucible made of bone ash), of about the same weight as the lead button or

a little heavier. The cupel is then placed in the muffle and again heated, with ready access of air. The lead melts and is oxidized; the resulting lead oxide melts at  $980^{\circ}$  C. and is absorbed by the porous cupel,\* while a kernel of silver and gold remains. The metallic kernel is flattened to foil and treated with nitric acid, which dissolves the silver, leaving the gold, usually in the form of powder. The gold is filtered off, dried, and melted, as above described, upon the charcoal stick. If the alloy of gold and silver (obtained after cupellation) contains three parts of silver to one part of gold, the gold remains after separation with nitric acid as a thin-as-paper, coherent, brownish mass (which becomes hard on igniting), with the characteristic gold color. If the proportion of silver to gold is greater than 3 : 1, the separation by means of nitric acid will be complete and the gold will be left as a powder. If the ratio of silver to gold is less than 3 : 1, the separation by means of nitric acid is incomplete, and the gold residue usually appears yellow, and still contains some silver. In this case, more silver is added, and one gm. of lead; the mixture is once more subjected to cupellation, when the subsequent separation by means of nitric acid will be complete.

In order to detect very small amounts of gold in ores, a similar procedure is used.

If one does not possess a muffle furnace, the tiresome wet process must be used. For example, if it is desired to detect the presence of gold in pyrites, a large amount of the ore is roasted in the air until all the sulphur has been burned off, then treated with bromine water, and allowed to stand twelve hours. The solution (which must now contain all of the gold as auric bromide) is filtered and the excess of bromine boiled off. Ferrous sulphate and a little sulphuric acid are now added, and the solution is again boiled and filtered through a small filter. The residue on the filter is washed and dried and then melted on the charcoal stick. According to the methods described, above a fractional part of a milligram of gold can be detected with certainty.

#### REACTIONS IN THE DRY WAY.

All compounds of gold, when heated with soda on the charcoal stick, yield a malleable, metallic button, soluble only in aqua regia.

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\* Considerable litharge is also volatilized.

The solution in the latter reagent should be evaporated, the residue dissolved in water and tested with stannous chloride, hydrogen peroxide, or zinc.

**PLATINUM, Pt. At. Wt. 195.2.**

Sp. Gr. = 21.48. M. Pt. = 1755° C.

*Occurrence.*—Platinum is found free in nature, usually accompanied by the other so-called platinum metals.

Metallic platinum is grayish white; in a finely-divided state it is grayish-black. The metal is not attacked by mineral acids; it dissolves only in aqua regia, forming chloroplatinic acid,  $\text{H}_2[\text{PtCl}_6]$  (not platinum chloride,  $\text{PtCl}_4$ ). If, however, the platinum is alloyed with silver, it dissolves in nitric acid to a yellow liquid, provided sufficient silver is present. Like tin, platinum forms two oxides:

Platinum monoxide, and Platinum dioxide,  
 $\text{PtO}$ ,  $\text{PtO}_2$ .

Both oxides may be obtained by the careful ignition of the corresponding hydroxides. They are exceedingly unstable, being decomposed by gentle ignition into metal and oxygen; all the remaining platinum compounds behave similarly.

The most important of the platinum compounds are the chlorides. By dissolving platinum in aqua regia, chloroplatinic acid is always obtained, from which the di- and tetrachlorides may be derived, which form with hydrochloric acid the complex acids

$\text{PtCl}_4 + 2\text{HCl} = \text{H}_2[\text{PtCl}_6]$  (Chloroplatinic acid—orange red crystals),

and

$\text{PtCl}_2 + 2\text{HCl} = \text{H}_2[\text{PtCl}_4]$  (Chloroplatinous acid—only known in solution).

The aqueous solution of chloroplatinic acid is yellowish-orange; on the other hand, a solution of chloroplatinous acid, containing the same amount of platinum as in the other case, is dark brown.

The potassium and ammonium salts of chloroplatinous acid are soluble in water; the corresponding salts of chloro-

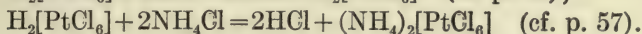
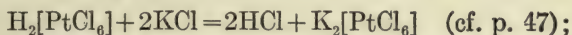


platinic acid are difficultly soluble in water and insoluble in 75 per cent. alcohol.

#### REACTIONS IN THE WET WAY.

A solution of chloroplatinic acid should be used for these reactions.

1. **Ammonium and Potassium Chlorides** produce in concentrated solutions a yellow precipitate:

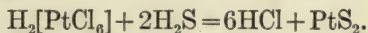


Both salts are difficultly soluble in water, but practically insoluble in 75 per cent. alcohol and in concentrated solutions of potassium and ammonium chlorides. This last property is utilized in separating platinum from gold and other metals.

2. **Alkali Iodides** give a brownish-red coloration when added to a solution of chloroplatinic acid:

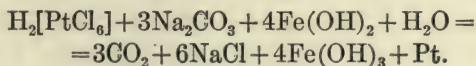


3. **Hydrogen Sulphide** precipitates in the cold very slowly, but quickly on warming, dark-brown platinum disulphide:



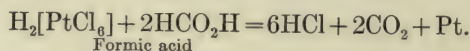
Platinum sulphide is insoluble in mineral acids, but readily soluble in aqua regia. It is difficultly soluble in alkali sulphides, but more readily soluble in alkali polysulphides, forming a sulpho salt, which is decomposable by acids, with precipitation of platinum sulphide.

4. **Ferrous Salts** do not reduce chloroplatinic acid in the presence of acids (difference from gold), but cause precipitation of all the platinum with ferric hydroxide (on warming) in a solution which has been neutralized with sodium carbonate:



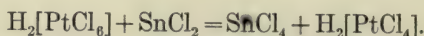
5. **Oxalic Acid** does not precipitate platinum (difference from gold).

6. **Formic Acid** precipitates from neutral boiling solutions all the platinum in the form of a black powder:

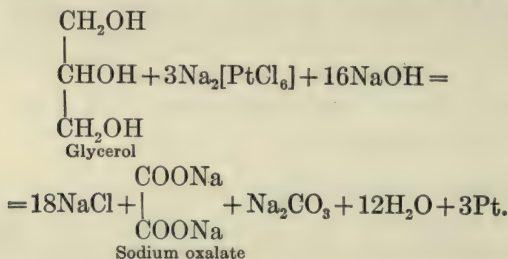


An acid solution must be neutralized with soda before making this test.

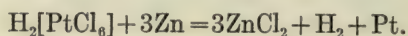
7. **Stannous Chloride** reduces chloroplatinic acid to chloroplatinous acid only, not to metal:



8. **Glycerol and Sodium Hydroxide** reduce chloroplatinic acid on warming, with the separation of the black, pulverulent metal:



9. **Zinc** reduces chloroplatinic acid to metal:



### Preparation of Chloroplatinic Acid for Use as a Reagent.

Since chloroplatinic acid is used not only for the qualitative detection of ammonium and potassium, but also for their quantitative separation, we will describe the methods for preparing a solution of this reagent

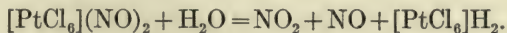
There are two cases to be considered, depending upon whether we start with metallic platinum or with platinum residues (precipitates of  $\text{K}_2[\text{PtCl}_6]$  etc.).

1. *Preparation of Chloroplatinic Acid from Metallic Platinum.*—Almost all commercial platinum contains iridium; and although pure iridium is practically insoluble in aqua regia, it dissolves considerably in this reagent if it is alloyed with platinum. Furthermore, platinum forms with aqua regia not only chloro-

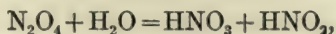
platinic acid, but also chloroplatinous acid (the most harmful of all impurities for this reagent) and nitroso-platinic chloride,  $[\text{PtCl}_6](\text{NO})_2$ . These facts must be borne in mind in preparing this reagent.

First of all, the platinum filings are purified by boiling with concentrated hydrochloric acid and washing with water. The platinum is then placed in a capacious flask, concentrated hydrochloric acid is poured over it, and nitric acid is added little by little, with continuous, gentle heating on the water-bath. All the platinum and some iridium are thus brought into solution, while small amounts of the latter metal usually remain undissolved as a black powder.

The solution is poured off (without stopping to filter) into a porcelain evaporating-dish and evaporated to syrup consistency. It is then dissolved in water, sodium formate and sodium carbonate are added until the solution is slightly alkaline; it is then heated to boiling, whereby the platinum and iridium are precipitated in a few minutes as a black powder. This operation should be performed in a large evaporating-dish, on account of the violent effervescence due to the escape of carbon dioxide. The supernatant liquid is now poured off and the residue washed several times with hydrochloric acid to remove the sodium salt, and finally with water in order to remove the acid. The powder, which contains iridium and platinum (in the presence of one another, but not alloyed together), is dried, strongly ignited in a porcelain crucible over the blast-lamp (whereby the iridium is made insoluble in the aqua regia), and weighed. The ignited gray metal is dissolved (at as low a temperature as possible) in hydrochloric acid, with a gradual addition of nitric acid. Considerable quantities of nitroso-platinic chloride are formed by this operation. On evaporating with water, this compound is decomposed into chloroplatinic acid, with evolution of the oxides of nitrogen:



As, however, a part of the  $\text{NO}_2$  (or  $\text{N}_2\text{O}_4$ ) remains in solution, some more nitric and nitrous acids are formed by the action of water,





which yields nitrosyl chloride with the hydrochloric acid present, and causes the formation of more nitroso-platinic chloride.

It is necessary, therefore, to evaporate the solution alternately with hydrochloric acid and with water until no more nitrous fumes are given off. The solution thus obtained always contains some chloroplatinous acid, and is intensely brown. In order to change the latter compound into chloroplatinic acid, the fairly-warm solution is saturated with chlorine gas (whereby its color becomes much lighter) and then evaporated (at as low temperature as possible) till it becomes of syrup consistency. After cooling, the syrup crystallizes to a yellowish-brown mass, which may be dissolved in a little cold water, and the insoluble iridium filtered off.

If there is a considerable amount of the latter metal, it is ignited in a porcelain crucible and weighed. The weight of the iridium should be deducted from the previous weight of the mixture, in order to find out how much platinum remains in solution.

The filtered solution is now diluted with water until 100 c.c. of the solution contains 10 gm. of platinum.

2. *Preparation of Chloroplatinic Acid from Platinum Residues.*—These residues consist of potassium chloroplatinate and the alcoholic wash-waters.

By evaporating an alcoholic solution of chloroplatinic acid, chloroplatinous acid and ethylene are formed, which yield ethylene platinous chloride; and the latter gives no precipitation with potassium or ammonium salts:



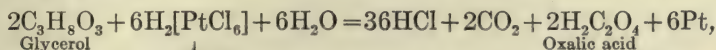
On evaporating an alcoholic solution of this soluble organic platinum compound, it is changed into an insoluble powder, explosive when dry, insoluble in acids, and completely decomposed by strong ignition only.

To separate platinum, therefore, from platinum residues, the alcoholic solution is, first of all, evaporated to dryness, taken up in water, and the solution poured into caustic soda (sp.gr. 1.2), to which 8 per cent. of glycerol\* has been added, the liquid heated

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\* Z. anal. Chem., 28, 509.

to boiling, causing the platinum to be precipitated as a heavy black powder,



which is washed, first, with water, then with hydrochloric acid, and finally with water again. The powder is dried, ignited (to destroy any of the organic compound), weighed, and transformed, as before, into chloroplatinic acid.

#### REACTIONS IN THE DRY WAY.

All platinum compounds, when heated with soda on charcoal, are reduced to the gray, spongy metal, which assumes a metallic lustre on being rubbed with a pestle in an agate mortar. It can be distinguished from gold by its color, and from lead, tin, and silver by its infusibility and insolubility.

#### Separation of Gold from Platinum.

The platinum is precipitated with a solution of ammonium chloride; after being filtered the solution is treated with ferrous sulphate to precipitate the gold.

### GROUP I. HYDROCHLORIC ACID GROUP.

To this group belong silver, mercury (in mercurous compounds), lead, thallium, and (under some circumstances) tungsten.

**SILVER**, Ag. At.Wt. 107.88.

Sp. Gr. = 10.5. M. Pt. = 960° C.

*Occurrence.*—Silver occurs both native and combined (chiefly with sulphur, arsenic, and antimony).

Of the silver-bearing minerals the following may be mentioned:

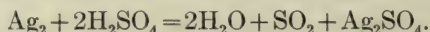
Horn silver,	Argentite,	Pyrargyrite, and	Proustite,
AgCl,	Ag <sub>2</sub> S,	Sb(SAg) <sub>3</sub> ,	As(SAg) <sub>3</sub> .

Silver is also found with tetrahedrite, and with galena.

Metallic silver is of a pure white color. It absorbs oxygen in the molten state, which it gives up (with tiny explosions) on cooling.

The proper solvent for silver is nitric acid. It is insoluble in

dilute hydrochloric and sulphuric acids, but dissolves readily in boiling sulphuric acid, with evolution of sulphur dioxide:



The solubility of silver in concentrated sulphuric acid is utilized in separating silver from gold and platinum in alloys.

Silver forms three oxides:

Silver suboxide,	Silver oxide,	Silver peroxide,*
$\text{Ag}_4\text{O}$ ,	$\text{Ag}_2\text{O}$ ,	$\text{Ag}_2\text{O}_2$ .

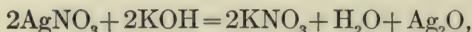
Of these oxides,  $\text{Ag}_2\text{O}$  alone is a basic anhydride; only one series of salts is known.

Silver oxide is a brownish-black powder, which on being heated to  $300^\circ$  is completely decomposed into metal and oxygen.

Most of the silver salts are colorless; the following, however, are colored: the bromide (yellow), the iodide (yellow), the sulphide (black), the phosphate (yellow), the arsenite (yellow), the arsenate (brown), and the chromate (reddish-brown). Most of the salts are insoluble in water, and are blackened on exposure to the light. The nitrate, chlorate, perchlorate, fluoride, nitrite, sulphate, and acetate are soluble in water, the last three with difficulty.

#### REACTIONS IN THE WET WAY.

**1. Potassium and Sodium Hydroxides** precipitate brown silver oxide,



insoluble in an excess of the precipitant, but readily soluble in nitric acid and in ammonia. If the solution in ammonia is allowed to stand, black detonating silver is deposited,  $[\text{AgNH}_3]_2\text{O}$ .

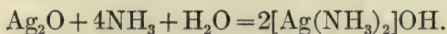
**2. Ammonia.**—If a neutral solution of a silver salt is cautiously treated with ammonia, the first drops produce a white precipitate,

\* Silver peroxide is formed at the anode during the electrolysis of a concentrated, aqueous solution of silver nitrate. The grayish-black crystalline powder has the composition:  $\text{Ag}_4\text{O}_4 = \text{Ag}_2\text{O} \cdot \text{Ag}_2\text{O}_3$  (Brauner and Kuzma, Ber., 1907, 3371). It may be regarded as the silver salt of the hypothetical

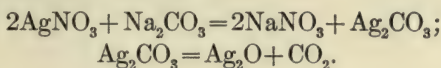
argentic acid,  $\text{Ag}-\text{OH}$ ; its symbol could then be written  $\text{Ag}[\text{AgO}_2]$ , analogous to the aurates, e.g.,  $\text{K}[\text{AuO}_2]$ .



which changes quickly to the brown oxide,  $\text{Ag}_2\text{O}$ . The greater part of the silver, however, remains in solution as silver ammonium nitrate,  $[\text{Ag}(\text{NH}_3)_2]\text{NO}_3$ ,\* and the oxide itself is dissolved by an excess of ammonia:

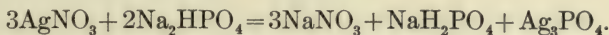


3. **Sodium Carbonate** precipitates white silver carbonate, which becomes yellow on being boiled, being slightly decomposed into oxide, with loss of carbon dioxide:

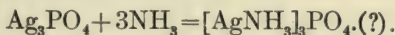


4. **Ammonium Carbonate** produces the same precipitate, but it is soluble in an excess of this reagent.

5. **Sodium Phosphate** throws down in neutral silver solutions a yellow precipitate of silver phosphate:

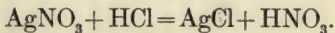


Silver phosphate is easily soluble in nitric acid and in ammonia. The solution of the phosphate in ammonia is due to the formation of a complex silver ammonium phosphate, perhaps



By neutralizing the ammoniacal solution with nitric acid, or the nitric acid solution with ammonia, the silver phosphate is reprecipitated.

6. **Hydrochloric Acid and Soluble Chlorides** precipitate from neutral and acid solutions white, curdy silver chloride:



Silver chloride is perceptibly soluble in pure water, particularly on boiling, but it is quite insoluble if an excess of silver nitrate or of hydrochloric acid is present (mass action, cf. p. 21, under Barium Sulphate).

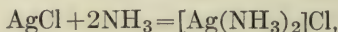
Silver chloride dissolves to a considerable extent in a large ex-

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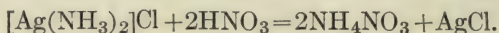
\* Cf. A. Reyhler, Chem. Zentralbl., 1904, I, p. 252.

cess of hydrochloric acid or of alkali chloride, while it is almost insoluble in dilute nitric acid.

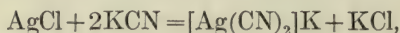
It is very soluble in ammonia,



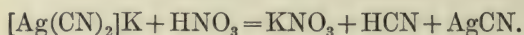
but is reprecipitated on addition of nitric acid to this solution:



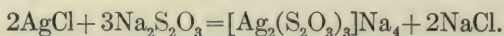
Silver chloride is also readily soluble in potassium cyanide solution,



and if such a solution is acidified, silver cyanide will be precipitated, with evolution of prussic acid:



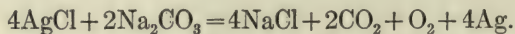
In the absence of acid, silver chloride is also readily soluble in a solution of sodium thiosulphate:



On boiling this solution, silver sulphide is precipitated.\*

Silver chloride is slowly attacked by boiling, concentrated sulphuric acid, with evolution of hydrochloric acid, and the formation of crystalline silver sulphate, insoluble in sulphuric acid.

By boiling with caustic soda or caustic potash solution, silver chloride is only partially decomposed; in the cold it is unaffected. Sodium carbonate solution does not affect it; but by fusing with sodium carbonate it is completely decomposed:



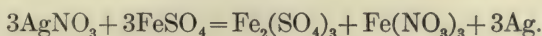
By fusing silver chloride itself a yellow liquid is obtained, which on cooling solidifies to a horny mass.

**7. Potassium Iodide** precipitates yellow, curdy silver iodide, practically insoluble in ammonia, but easily soluble in potassium cyanide and sodium thiosulphate solutions.

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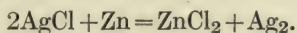
\* If considerable  $\text{Na}_2\text{S}_2\text{O}_3$  is present, the precipitation of  $\text{Ag}_2\text{S}$  takes place slowly, but more quickly after diluting the solution.

8. **Ferrous Sulphate** precipitates gray metallic silver from boiling solutions:

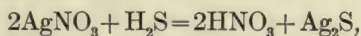


Frequently a basic ferric salt is precipitated at the same time, particularly from very dilute solutions.

9. **Zinc**, having a greater solution pressure than silver, precipitates the latter from neutral solutions. Similarly, if insoluble silver chloride is covered with dilute sulphuric acid and a piece of zinc placed in contact with the chloride, the latter will be reduced to metal.

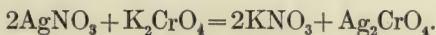


10. **Hydrogen Sulphide** precipitates from neutral, ammoniacal, and acid solutions black silver sulphide,

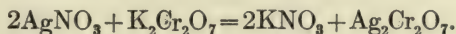


insoluble in ammonia, alkali sulphides, and dilute potassium cyanide solution. Silver sulphide is perceptibly soluble in a concentrated solution of potassium cyanide,\* and easily soluble in hot dilute nitric acid, with separation of sulphur and formation of silver nitrate.

11. **Potassium Chromate** precipitates brownish-red silver chromate, soluble in ammonia and in nitric acid.



12. **Potassium Dichromate** precipitates reddish-brown silver dichromate soluble in ammonia and in nitric acid:†



#### REACTIONS IN THE DRY WAY.

Fused with soda on charcoal, all silver compounds yield a white, malleable, metallic button without incrustation (difference from

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\* If a considerable amount of concentrated potassium cyanide solution is mixed with a silver solution, and dilute hydrogen sulphide added, no precipitate is formed at first; but gradually silver sulphide is produced, and with more hydrogen sulphide the silver is all precipitated.

† W. Autenrieth, Ber. 35, 2058 (1902).



lead and tin), readily soluble in nitric acid (difference from tin). The solution is not precipitated by very dilute sulphuric acid, but is immediately precipitated by hydrochloric acid (difference from lead).

The reactions of lead and mercurous compounds have already been described (pp. 176, 182).

### **Separation of Silver, Lead, and Mercurous Compounds.**

The chlorides of these three metals are precipitated by hydrochloric acid. [Lead is partly found in the filtrate, and is, therefore, always tested for in the hydrogen sulphide group.] The chlorides are filtered, washed with a little cold water, boiled with a considerable quantity of water, and filtered hot.

RESIDUE:  $[\text{AgCl}, \text{Hg}_2\text{Cl}_2]$ .

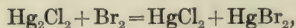
It is treated with ammonia and filtered: \*

Residue:	Solution:
$\text{Hg} \begin{smallmatrix} \text{NH}_2 \\ \text{Cl} \end{smallmatrix} + \text{Hg}$ , black, showing presence of <i>mer-</i> <i>cury</i> .	$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ . It is acidified with $\text{HNO}_3$ , when a white precip- itate of $\text{AgCl}$ shows the pres- ence of <i>silver</i> .

SOLUTION:  $\text{PbCl}_2$ .

On cooling the solution, crystals of lead chloride will separate out if considerable lead is present. The solution is treated with dilute sulphuric acid, whereby difficultly soluble white lead sulphate is formed; or it is treated with potassium dichromate solution, when a yellow precipitate shows the presence of *lead*.

\* According to A. Thiel (Allgem. chem. Zeit., 1904) a small amount of silver chloride in the presence of considerable mercurous chloride cannot be dissolved by means of ammonia. Thiel, therefore, first treats the chlorides of silver and mercury with bromine water, thereby oxidizing the mercurous salt,



which goes into solution, leaving the silver chloride behind. The latter is filtered off, dissolved in ammonia, and tested as above.

## REACTIONS OF THE METALLOIDS (ANIONS).

In order to detect a metalloid, it is almost always necessary to get it in the form of an acid. The acids, as well as their salts, are always more or less dissociated into electropositive cations, and electre-negative anions. Up to this point we have concerned ourselves chiefly with the study of the cations. In the following section of the book we shall study the behavior of the anions.

The presence of *hydrogen ions* in aqueous solutions is the characteristic of all acids; upon it alone the acid reaction depends.\* In the Introduction (p. 28) we have mentioned methyl orange † as a typical reagent which can be used in testing for hydrogen ions. There are other organic dyestuffs which undergo a corresponding change of color on coming in contact with hydrogen ions, and which may be used as acid indicators. Among these substances are litmus and lacmoid (colored red by acids), congo red (changing to blue), etc.

### DIVISION OF THE ACIDS INTO GROUPS.

The classification of the acids which we prefer was first published by R. Bunsen in 1878 (in manuscript form) for the use of his students; it was adopted (with his consent) by V. Meyer and the author in their "Tabellen zur qualitativen Analyse." This

\* Acids are known which are scarcely dissociated at all in aqueous solution. Such acids scarcely show the characteristic acid properties. The strength of an acid in solution, from a physico-chemical point of view, depends upon the extent to which it is dissociated, but it must be borne in mind that this bears no relation to the quantity of alkali which can be neutralized. Thus one equivalent of the comparatively weak acetic acid will neutralize one equivalent of caustic alkali because as fast as the  $H^+$  ions are neutralized by the  $OH^-$  ions from the alkali, more of the former are formed from the acid because the original state of equilibrium between  $H^+$  ions and undissociated acid has been disturbed. Confusion has arisen in the literature because in some cases the *acidity* of a solution has been measured by the quantity of  $H^+$  ions present at the start and in other cases by the quantity of alkali which the solution will neutralize.

† Methyl orange, or helianthine, is dimethylamidoazobenzenesulphonic acid,  $\left[ \begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix} > C_6H_4-N=N-C_6H_4SO_3 \right] H..$  This acid contains both acid and base-forming groups and the molecule undergoes a rearrangement of the atoms when treated with a base, whereby the chromophor (color-producing group) is changed and the color turns from red to yellow. The sodium salt of methyl orange is ordinarily used as indicator; it behaves as a very weak base.

classification is based upon the different solubilities of the barium and silver salts of the different acids.

#### GROUP I

includes those acids whose *silver salts* are *insoluble* in *water* and in *nitric acid*, but whose *barium salts* are *soluble* in *water*.

To this group belong hydrochloric, hydrobromic, hydriodic, hydroferrocyanic, hydroferriecyanic, sulphocyanic, and hypochlorous acids.

#### GROUP II

contains those acids whose *silver salts* are *soluble* in *nitric acid*, but are *insoluble*, or *difficultly soluble*, in *water*, and whose *barium salts* are *soluble* in *water*.

To this group belong hydrosulphuric, hydroselenic, hydrotelluric, nitrous, acetic, cyanic, and hypophosphorous acids.

#### GROUP III.

comprises those acids whose *silver salts* are *white* and *soluble* in *nitric acid*, but whose *barium salts* are *difficultly soluble* or *insoluble* in *water*, but *soluble* in *nitric acid*.

To this group belong sulphurous, selenous, tellurous, phosphorous, carbonic, oxalic, iodic, boric, molybdic (selenic and telluric), tartaric, citric, meta- and pyrophosphoric acids.

#### GROUP IV

contains those acids whose *silver salts* are *colored* and *soluble* in *nitric acid*, but whose *barium salts* are *insoluble* in *water* and *soluble* in *nitric acid*.

To this group belong phosphoric, arsenic, arsenious, vanadic, thiosulphuric, chromic, and periodic acids.

#### GROUP V

comprises those acids whose *silver* and *barium salts* are *soluble* in *water*.

To this group belong nitric, chloric, perchloric, and the man-  
ganic acids.

#### GROUP VI

comprises those acids whose *silver salts* are *soluble* in *water*, but whose *barium salts* are *insoluble* in *nitric acid*.

To this group belong sulphuric, hydrofluoric, and hydrofluosilicic acids.



## GROUP VII

contains non-volatile acids, which form soluble salts with the alkalis alone.

To this group belong silicic, tungstic, titanio, niobic, tantalic, and zirconic acids.

## GROUP I.

**Silver Nitrate** produces a precipitate insoluble in nitric acid.

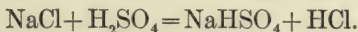
**Barium Chloride** causes no precipitation.

## HYDROCHLORIC ACID, HCl.

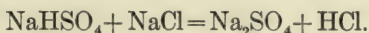
*Occurrence.*—Hydrochloric acid is found free in nature, but in small quantities (for example, in the exhalations of active volcanoes); its salts, however, are exceedingly common, especially those with the alkalis. (See these.)

*Preparation.*—Hydrochloric acid is set free by the action of concentrated sulphuric acid upon any chloride. Ordinary rock salt is usually used, it being the cheapest chloride.

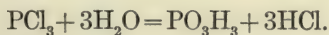
If sulphuric acid is allowed to act upon ordinary salt, a considerable evolution of hydrochloric acid takes place even in the cold, with the formation of monosodium sulphate.\*



And, on warming, the monosodium sulphate reacts with more sodium chloride:



Hydrochloric acid may also be prepared by the action of water on many acid chlorides:

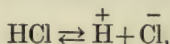


*Properties.*—Hydrochloric acid is a colorless gas, with a suffocating odor, and forms dense clouds in moist air. It is readily solu-

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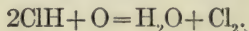
\* When only one hydrogen of a dibasic acid is replaced by metal, the resulting salt is usually designated by placing the prefix *bi* before the name of the acid; sodium bicarbonate,  $\text{NaHCO}_3$ ; sodium bisulphate,  $\text{NaHSO}_4$ , etc. There is *twice* as much acid per equivalent of base as in the case of the normal salt.

ble in water (one volume of water dissolves, at 18° C., 451 volumes of hydrochloric acid). The sp. gr. of the saturated aqueous solution is 1.21, and 100 gm. of this solution contains 42.3 gm. of hydrochloric acid gas. The ordinary commercial hydrochloric acid is of sp. gr. 1.18 to 1.19, and contains 36 to 38 per cent of the gas. The aqueous solution of hydrochloric acid is one of our strongest acids. In dilute solution it is almost entirely dissociated,



so that such a solution is a good conductor of electricity.

*The behavior of hydrochloric acid on oxidation is extremely characteristic; water is formed and chlorine is set free:*

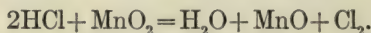


This oxidation will not take place on exposure to atmospheric, or even pure, oxygen, but only by nascent oxygen under certain definite conditions.

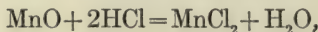
Thus the following classes of substances will oxidize concentrated hydrochloric acid (sometimes in the cold): *The peroxides of the heavy metals,\* all nitrates, nitrites, chlorates, hypochlorites, chromates, selenates, and tellurates.*

#### 1. Oxidation of Hydrochloric Acid by Means of Peroxides.

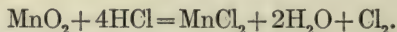
(a) *By manganese dioxide:*



One atom of oxygen from the manganese dioxide molecule is available for oxidation. The manganese dioxide is reduced to manganese monoxide; and the latter, being the anhydride of a base, unites with more of the hydrochloric acid to form manganous chloride:

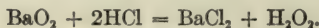


so that the whole reaction may be represented by the following equation:

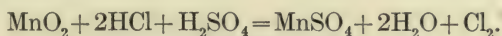



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\* The peroxides of the light metals do not yield chlorine, but hydrogen peroxide:

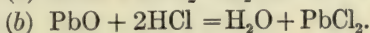
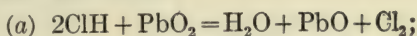


Some other acid, preferably sulphuric, can be used for the neutralization of the manganese monoxide, so that the yield of chlorine from a given quantity of hydrochloric acid will be twice as large:

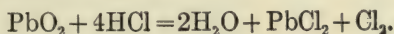


In the former case only half of the chlorine from the hydrochloric acid was set free; in the latter the total chlorine becomes available.

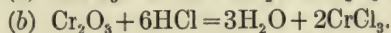
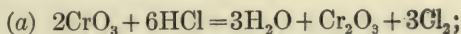
(b) *By lead peroxide:*



Total reaction:



(c) *By chromium trioxide:*

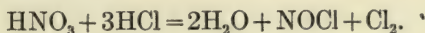


Total reaction:



## 2. Oxidation of Hydrochloric Acid by Nitric Acid, etc.

When concentrated nitric acid acts upon concentrated hydrochloric acid, the products of the reaction are water, nitrosyl chloride and free chlorine:



In this reaction the valence of the nitrogen has been reduced from five to three, and two atoms of chlorine have been oxidized to form an electrically neutral chlorine molecule.

A mixture of one molecule of nitric acid with three of hydrochloric acid is known as

*Aqua Regia*.—The acids are usually mixed, not according to their weights, but according to their volumes.



Aqua regia is, therefore, chlorine water, with the distinction that the chlorine exists in the nascent state; which explains why aqua regia is a much more energetic reagent than ordinary chlorine water. Nitrous acid, chloric acid, hypochlorous acid, selenic and telluric acids all act similarly with hydrochloric acid.

Hydrochloric acid is *monobasic*; its salts are called *chlorides*.

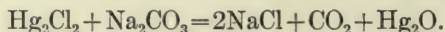
### *Solubility of Chlorides.*

Nearly all chlorides are soluble in water, but the following are insoluble:

Mercurous chloride, $\text{Hg}_2\text{Cl}_2$ .	Aurous chloride, $\text{AuCl}$ .
Silver chloride, $\text{AgCl}$ .	Platinous chloride, $\text{PtCl}_2$ .
Cuprous chloride, $\text{Cu}_2\text{Cl}_2$ .	Bismuth oxychloride, $\text{BiOCl}$ .
Lead chloride, $\text{PbCl}_2$ .	Antimony oxychloride, $\text{SbOCl}$ .
Thallium chloride, $\text{TlCl}$ .	Mercuric oxychloride, $\text{Hg}_2\text{Cl}_2\text{O}$ .

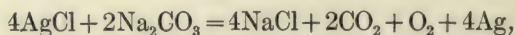
Of these chlorides which are insoluble in water all, with the exception of silver chloride, aurous chloride, and platinous chloride, are soluble in strong hydrochloric acid. They are all soluble in aqua regia, with the exception of silver chloride.

By boiling these insoluble chlorides in a concentrated solution of sodium carbonate, all, with the exception of silver chloride again, are readily decomposed; *e.g.*:



By filtration a chloride solution is obtained which is free from heavy metal.

By fusing with sodium carbonate, even silver chloride is decomposed,



and silver chloride may also be decomposed by nascent hydrogen (cf. p. 273).

The deliquescent chlorides (lithium, calcium, and strontium) are all soluble in absolute alcohol and in amyl alcohol.

The chlorides of potassium, sodium, and barium are quite insoluble in concentrated hydrochloric acid; they can, therefore, be easily separated from the remaining chlorides which are

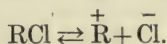
soluble in water by saturating the solution with hydrochloric acid gas.

Most all chlorides are insoluble in ether, with the exception of mercuric, stannous, stannic, auric, and ferric chlorides.

#### REACTIONS OF CHLORIDES IN THE WET WAY.

A neutral solution of an alkali chloride should be used for these reactions.

Like hydrochloric acid, most chlorides are practically completely dissociated in dilute aqueous solution:

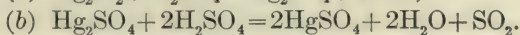
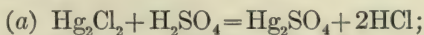


The chlorine of hydrochloric acid (or the soluble chloride) is present in the form of the chlorine ion. It is, therefore, a matter of indifference which chloride we take for the following reactions, provided there is no independent reaction taking place due to the presence of the cation. If an alkali chloride is used such reactions will not take place, consequently a neutral alkali salt is usually used for the anion test.

1. **Dilute Sulphuric Acid** (1 : 10) produces no reaction, even on warming.

2. **Concentrated Sulphuric Acid** \* decomposes the chloride almost completely in the cold, completely on warming. Sulphate and colorless hydrochloric acid gas result from this reaction; and the latter is easily recognized by its odor, by the clouds which it forms in moist air or with ammonia vapors (obtained by holding a glass rod wet with ammonia near the test-tube), and by its turning moist blue litmus-paper red. Water is not made turbid by hydrochloric acid (difference from hydrofluosilicic acid).

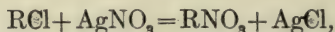
Silver chloride and mercurous chloride are decomposed with difficulty by sulphuric acid, the latter with evolution of sulphur dioxide; the *mercurous* sulphate (which is at first formed) is oxidized (at the expense of the oxygen of the sulphuric acid) to *mercuric* sulphate:




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\* This reaction is best performed with a solid chloride in a small test-tube.

3. **Silver Nitrate** produces a white, curdy precipitate of silver chloride,

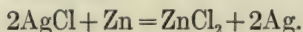


insoluble in nitric acid, soluble in ammonia, potassium cyanide, and sodium thiosulphate solutions. (See Silver.)

From a solution of silver chloride in ammonia, acids reprecipitate silver chloride. From a solution in potassium cyanide, acids precipitate silver cyanide. If it is desired to test a solution of ferrous sulphate for the presence of a small amount of chloride, it must be strongly acidified with nitric acid, as otherwise a precipitate of metallic silver will be obtained, which may cause confusion (cf. p. 273). The best way to test the solution of ferrous sulphate for hydrochloric acid is to add sodium carbonate solution until alkaline, boil, and filter. In the filtrate the acids originally present are now in the form of their sodium salts, in the presence of an excess of sodium carbonate; and the latter should be neutralized with nitric acid before the silver nitrate is added.

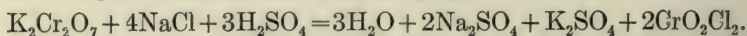
The detection of chloride when present in the form of chloride of a heavy metal is accomplished in a similar manner; and, with the exception of silver chloride, any insoluble chloride may be decomposed in the same way, by boiling with sodium carbonate solution.

In order to confirm the presence of chlorine in silver chloride, it is treated with dilute sulphuric acid, a piece of zinc added, and after a little while the solution is poured off from the deposited silver and tested with silver nitrate:

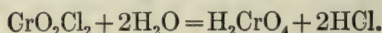


Or, the silver chloride is fused with sodium carbonate, the melt extracted with water, filtered, acidified with nitric acid, and tested with silver nitrate.

4. **Potassium Dichromate and Sulphuric Acid.**—If a dry chloride is mixed with potassium dichromate, concentrated sulphuric acid added, and the mixture heated in a small retort, brownish vapors are given off which are condensed, in the receiver, to a brown liquid (chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ ):



Chromyl chloride is an acid chloride, and is, therefore, decomposed by water into chromic and hydrochloric acids:



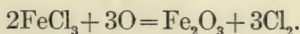


On adding caustic soda or potash, an alkali chloride and a yellow alkali chromate are obtained. If the solution is then acidified, some ether and a little hydrogen peroxide added, and the liquid shaken, the upper ether layer will be colored blue, showing the presence of chromium; and the presence of chromium indicates that a chloride was originally present (difference from bromide and iodide).

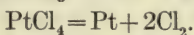
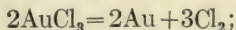
### Behavior of Chlorides on Ignition.

The chlorides of the alkalis and alkaline earths melt (without perceptible decomposition) on being heated in the air.

The chlorides of the sesquioxides are decomposed, more or less completely, on being ignited in the air. Thus, ferric chloride is almost quantitatively decomposed into ferric oxide, with loss of chlorine:



The chlorides of gold and of the platinum metals are readily decomposed into chlorine and metal:

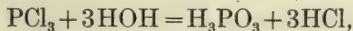


The remaining chlorides are mostly volatile, without perceptible decomposition.

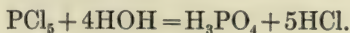
### Detection of Chlorine in Non-electrolytes.

Besides uniting with metals and with hydrogen, chlorine also forms compounds with the metalloids; *e.g.*,  $\text{PCl}_3$ ,  $\text{PCl}_5$ ,  $\text{AsCl}_3$ ,  $\text{AsCl}_5$ ,  $\text{SbCl}_3$ ,  $\text{SbCl}_5$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , etc.

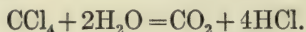
All these compounds, which may be regarded as acid chlorides, are decomposed by water with the formation of hydrochloric acid, which can be tested for in the usual way. The hydrolysis usually takes place at the ordinary temperatures. Thus, phosphorus trichloride yields with water phosphorous acid and hydrochloric acid,



and phosphorus pentachloride yields phosphoric acid and hydrochloric acid:



The remaining acid chlorides are decomposed in a similar way by water at the ordinary temperature, with the exception of carbon tetrachloride, which is only decomposed by heating with water in a closed tube as follows:



Chlorine acts upon a great many hydrocarbons, forming substitution products which are non-electrolytes, and consequently will not give the chloride tests; for example, if chloroform,  $\text{CHCl}_3$ , is shaken with a solution of aqueous silver nitrate, it will not yield a precipitate of silver chloride. In order to test such compounds for chlorine (as is frequently necessary in the study of organic compounds), the chlorine must be changed to hydrochloric acid by one of the following methods:

1. **Carius' Method.**—By heating the compound in a sealed glass tube with concentrated nitric acid, in the presence of silver nitrate, the compound is completely decomposed, and all the chlorine is changed to silver chloride, which can be filtered off; and, after treatment with zinc and dilute sulphuric acid, can be tested as above.\*

2. **By Heating with Lime.**—A layer of granular lime (free from chloride), then a mixture of the substance to be tested with lime, and finally another layer of lime are placed in a small glass tube, which should be about 25 cm. long and about 1 cm. wide.

By gently tapping the tube, a canal is opened between the upper wall of the tube and the substance, through which the gases evolved may escape. The tube is then placed horizontally in a small combustion furnace and heated (first the front layer of lime, then the back layer, and finally the entire contents of the tube) to a dull red heat.

By this means the organic substance will be completely decomposed, and the chlorine will be found combined with the lime in the form of calcium chloride.

After cooling, the contents of the tube should be dissolved in dilute nitric acid, the carbon filtered off, and the filtrate tested with silver nitrate for chlorine ions.

3. **Treatment with Sodium.**—A small amount of the dry substance to be tested is placed in a small test-tube, a small piece of sodium (freed from petroleum) is added, and the metal covered

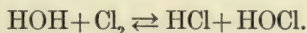
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\* The precautions to be taken in sealing and opening the tube are described in Vol. II.

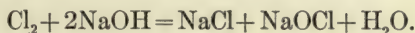
with another layer of the substance. The tube is then heated in the gas-flame, the decomposition taking place suddenly with incandescence. The still hot tube is transferred to a small beaker containing water [which breaks the tube] and sodium chloride dissolves with other sodium compounds. The solution is filtered, acidified with nitric acid, and then tested with silver nitrate for halogens.

### FREE CHLORINE.

Chlorine (produced by the oxidation of hydrochloric acid or by igniting various chlorides) is a greenish-yellow gas, with a suffocating odor. It is absorbed by water (one volume of water absorbs at 10° C. about 2.7 volumes of chlorine gas), forming chlorine water, a yellowish-green liquid, and a poor conductor of electricity (although better than pure water, showing that some ions are present). Chlorine probably decomposes water to a slight extent, forming hydrochloric acid and hypochlorous acid:

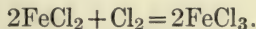


If the acids formed are removed by the addition of alkali, the reaction proceeds quantitatively in the direction from left to right:

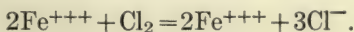


Chlorine water is a strong oxidizing agent (cf. p. 4), which can be explained by assuming that water is decomposed by the chlorine, forming hydrochloric acid and setting free oxygen.

It may also be assumed that hypochlorous acid is first formed. Neither of these assumptions is necessary, as the conversion of neutral chlorine into negatively charged chlorine ions is a reduction and must always be accompanied by an oxidation of some other element:



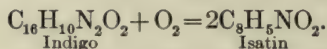
or



This decomposition of chlorine water takes place slowly in the dark, but more rapidly in the light, and in the presence of oxidizable substances. The bleaching action of chlorine water depends



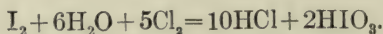
upon this oxidizing action. Thus, indigo solution is decolorized, the indigo being oxidized to isatin:



If a solution of potassium iodide is treated with chlorine water, iodine is set free, and the solution turns yellow to brown:

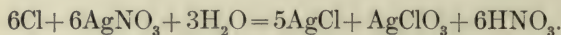


If the yellow solution is shaken with carbon disulphide, or chloroform, the iodine is absorbed by these reagents and they assume a reddish-violet color. By the addition of more chlorine water the solution becomes colorless, owing to the oxidation of the iodine to colorless iodic acid:

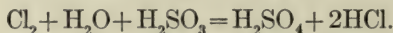


The free iodine can also be detected by the addition of some starch paste (instead of carbon disulphide, etc.), which is turned blue by iodine.

1. **Silver Nitrate** gives a white precipitate of silver chloride in chlorine water; but this precipitation is not quantitative, for one sixth of the chlorine is changed into soluble silver chlorate:

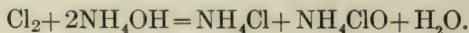


On adding a slight excess of sulphurous acid to chlorine water the chlorine is readily and completely changed into hydrochloric acid:

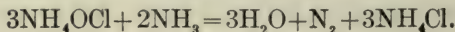


From this solution the chlorine can be precipitated quantitatively by a silver solution.

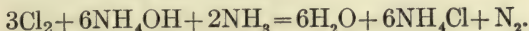
Chlorine may also be easily changed into the form of a chloride by the addition of ammonia. At first, ammonium chloride and ammonium hypochlorite are formed:



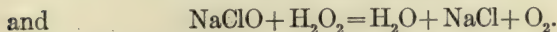
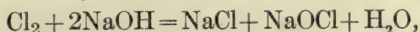
The ammonium hypochlorite immediately oxidizes more of the ammonia, with evolution of nitrogen:



The total reaction is, therefore,



Chlorine can be changed to a chloride by the action of hydrogen peroxide in the presence of sodium or potassium hydroxide:

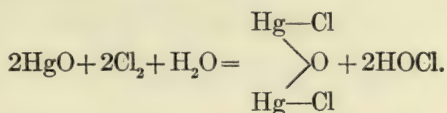


**2. Metallic Mercury** is attacked by chlorine at the ordinary temperature, forming insoluble mercurous chloride.

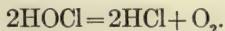
If therefore chlorine water is shaken with metallic mercury until it no longer smells of chlorine, a neutral solution is obtained which contains no chlorine. If hydrochloric acid is present, the solution now reacts acid, and gives a precipitate with silver nitrate, for metallic mercury is not attacked by hydrochloric acid. This reaction is made use of in testing for hydrochloric acid in the presence of chlorine.

### HYPOCHLOROUS ACID, HOCl.

*Preparation.*—A solution of free hypochlorous acid is obtained by shaking chlorine water with yellow mercuric oxide until the solution no longer smells of chlorine:



Brown, insoluble mercuric oxychloride is formed by the reaction, and the solution contains hypochlorous acid. If the solution is poured off from the insoluble basic mercuric salt, and distilled, a pure solution of hypochlorous acid will be obtained; which, however, cannot be kept long in the light, for it decomposes into hydrochloric acid and oxygen:



Hypochlorous acid is a vigorous bleaching agent; litmus and indigo are quickly decolorized.

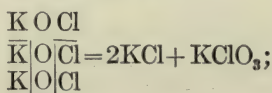
The alkali salts of hypochlorous acid (hypochlorites) are ob-

tained by neutralizing the acid with dilute sodium or potassium hydroxide; or, more conveniently, by the action of chlorine on a dilute caustic alkali solution:



The ammonium salt cannot be prepared, because it is immediately decomposed, acting upon the excess of ammonia present (cf. p. 286).

All hypochlorites are readily changed, on warming, into chlorate\* and chloride (cf. p. 143 foot note):



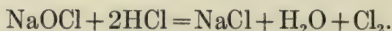
consequently hypochlorites must always be prepared in cold dilute solution.

The most important commercial hypochlorite is the so-called "chloride of lime," which is obtained by passing chlorine gas over lime at the ordinary temperature.

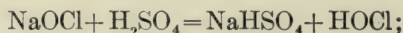
#### REACTIONS IN THE WET WAY.

All hypochlorites are soluble in water, and are decomposed by acids (carbonic acid even).

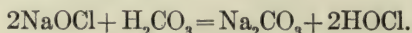
1. **Hydrochloric Acid** is oxidized by hypochlorites with evolution of chlorine:



2. **Sulphuric Acid** decomposes hypochlorites, setting free hypochlorous acid:



and carbonic acid acts similarly:



It is due to the fact that the hypochlorites are so readily decomposed with the formation of chlorine that they act as strong bleaching agents; indigo solution (a solution of indigo in sulphuric acid) being immediately decolorized.

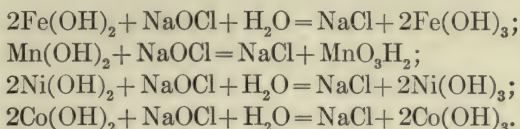
Hypochlorites act as oxidizing agents not only in acid solutions,

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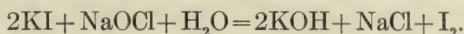
\* In the presence of 40% or more of caustic potash the potassium hypochlorite on being heated decomposes into chloride with evolution of oxygen and the formation of no perchlorate (F. Winteler, *Z. angew. Chem.*, **33** (1902), p. 778).



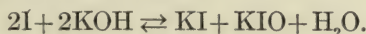
but also in alkaline solutions at ordinary temperatures (difference from chlorates); many metallic hydroxides being oxidized by them to higher hydroxides. Thus, ferrous hydroxide is readily oxidized to reddish-brown ferric hydroxide; manganous, nickelous, and cobaltous hydroxides are oxidized to brownish-black hydroxides:



**3. Iodo-Starch Paper** is turned blue by hypochlorites in weakly alkaline solutions, owing to the separation of iodine:

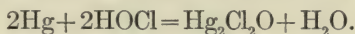


This reaction is not quantitative, because the iodine reacts, to some extent, upon the potassium hydroxide, forming potassium hypoiodite and potassium iodide:



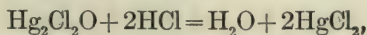
But as this reaction is reversible, the extent to which it takes place must depend upon the concentration of the potassium hydroxide; and in dilute solutions enough iodine will be present to produce the blue coloration with the starch.

**4. Metallic Mercury.**—If a solution containing free hypochlorous acid is shaken with metallic mercury, brown basic mercuric chloride is formed, insoluble in water, but soluble in hydrochloric acid:



Under these same conditions free chlorine forms, on being shaken with mercury, white mercurous chloride, which is insoluble in hydrochloric acid.

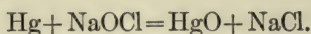
This property is utilized in detecting hypochlorous acid in the presence of free chlorine. The mixture is shaken with mercury until a little of the solution no longer turns iodo-starch paper blue; the liquid is then carefully poured off, hydrochloric acid is added to the residue, and the mixture is shaken, when the basic chloride produced by hypochlorous acid goes into solution:



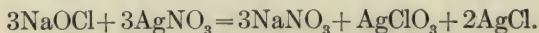
while mercurous chloride remains undissolved.

If hydrogen sulphide is passed into the filtered solution, the formation of mercuric sulphide shows that hypochlorous acid was originally present.

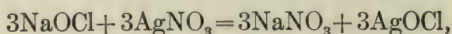
The salts of hypochlorous acid behave differently towards mercury than is the case with the free acid; they form insoluble mercuric oxide and a soluble chloride:



5. **Silver Nitrate** causes in solutions of hypochlorites an incomplete precipitation of silver chloride. One third of the chlorine remains in solution in the form of chlorate:



First of all, the unstable silver hypochlorite is formed:



which is immediately decomposed into chlorate and chloride:

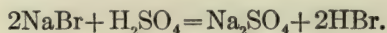


Hypochlorous acid is distinguished from chlorine by its behavior towards mercury; from hydrochloric acid by its oxidizing action; and from chloric acid by its being partly precipitated by silver nitrate, and by its oxidizing action in alkaline solutions.

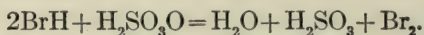
### HYDROBROMIC ACID, HBr.

*Occurrence.*—Bromine compounds are constantly found in nature in company with those of chlorine; so that salts of hydrobromic acid are found in the ocean and in many mineral waters.

*Preparation.*—Hydrobromic acid is formed by the action of sulphuric acid upon a bromide:



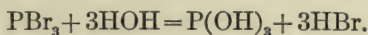
But the hydrobromic acid obtained by means of this reaction is never pure, being contaminated with bromine; a part of the hydrobromic acid is oxidized by the sulphuric acid:



The more concentrated the sulphuric acid used, the larger will be the yield of bromine.

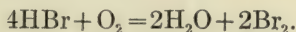
If dilute sulphuric acid ( $3\text{H}_2\text{SO}_4 : 1\text{H}_2\text{O}$ ) is used, the hydrobromic acid obtained is almost free from bromine.

Pure hydrobromic acid may be obtained by the action of an acid bromide upon water:

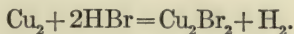


*Properties.*—Hydrobromic acid (like hydrochloric acid) is a colorless gas with a suffocating odor, having the property of fuming in moist air and forming clouds of ammonium bromide with vapors of ammonia. It is very soluble in water. The concentrated solution has the sp. gr. 1.78 and contains 82 per cent of hydrobromic acid. The affinity of bromine for hydrogen is greater than that of iodine, but less than that of chlorine.

While hydrochloric acid can be kept in aqueous solution for an indefinitely long time, a solution of hydrobromic acid soon turns brown, owing to the separation of bromine. Hydrobromic acid is oxidized by atmospheric oxygen:



As hydrobromic acid is so easily decomposed into its elements, it attacks metals readily, even metals which are unattacked by hydrochloric acid. Thus, bright copper is promptly dissolved by hydrobromic acid, with evolution of hydrogen and formation of cuprous bromide:



As hydrobromic acid is oxidized by atmospheric oxygen, it follows that it is much more readily oxidized by nascent oxygen. Thus, it is oxidized, with separation of bromine, by peroxides, nitrates, nitrites, chromates, etc., provided a concentrated solution of hydrobromic acid is used.

Hydrobromic acid is a monobasic acid; its salts are called bromides.

The solubility of a bromide is about the same as that of the corresponding chlorine compound.



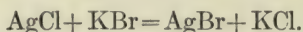
## REACTIONS IN THE WET WAY.

1. **Dilute Sulphuric Acid** (1 : 10) evolves no hydrobromic acid from bromides in the cold, but does so on warming from bromides of the alkalis.

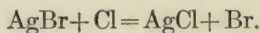
2. **Concentrated Sulphuric Acid** causes evolution of hydrobromic acid and bromine from all bromides. The solution is brown, and, on warming, yellowish-brown vapors are given off (difference from hydrochloric acid); which, as they contain hydrobromic acid, fume in moist air, have a suffocating odor, and do not render water turbid (difference from hydrofluosilicic acid).

3. **Silver Nitrate** produces a curdy, yellowish precipitate of silver bromide, insoluble in nitric acid, but soluble in ammonia, potassium cyanide, and sodium thiosulphate.

If silver chloride is digested with potassium bromide, the former will be changed into silver bromide:



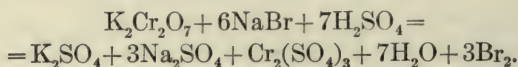
If, however, silver bromide is heated and treated with chlorine, it is readily changed into silver chloride:



4. **Chlorine Water**, on being added to solutions of soluble bromides, sets free bromine, which is soluble in carbon disulphide or chloroform, forming a brown solution; but it is changed, by an excess of chlorine water, into yellowish chloride of bromine ( $\text{BrCl}$ ) (difference from iodine).

5. **Potassium Dichromate**, in the presence of dilute sulphuric acid, effects no separation of bromine from aqueous solutions of bromides; on shaking the solution with carbon disulphide, the latter remains colorless (difference from iodine).

6. **Potassium Dichromate and Concentrated Sulphuric Acid**—On mixing a solid bromide with solid potassium dichromate, covering the mixture with concentrated sulphuric acid and distilling, a brown distillate is obtained (as with a chloride), which, however, consists of bromine and contains no chromium:



On adding dilute sodium hydroxide to the distillate, a colorless (or sometimes a faint yellow) solution is obtained; which, after being acidified with sulphuric acid, does not give the chromium reaction with dilute sulphuric acid and hydrogen peroxide, but merely turns brown owing to the liberation of free bromine (difference from chlorine).

7. **Nitrous Acid** does not cause the separation of bromine from a dilute bromide solution in the cold (difference from iodine).

### Detection of Bromine in Non-electrolytes.

The method of procedure is exactly the same as was given in the case of chlorine in a non-electrolyte (see page 284).

### FREE BROMINE.

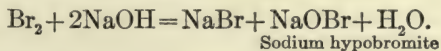
Free bromine (which may be obtained by the oxidation of hydrobromic acid) is a brown liquid at the ordinary temperature, and dissolves in water, forming a colored solution. The cold saturated solution of bromine contains 2-3 per cent of dissolved bromine. Concentrated hydrochloric acid at the ordinary temperatures dissolves much more bromine, the saturated solution containing about 13 per cent of the substance.

Bromine, like chlorine, acts as a strong bleaching agent (oxidizing the color) and combines directly with metallic mercury, forming insoluble mercurous bromide.

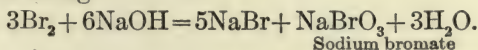
The detection of hydrobromic acid in the presence of bromine is accomplished in precisely the same way as was described for the detection of hydrochloric acid in the presence of free chlorine (cf. p. 287).

Bromine acts upon the alkalies exactly as chlorine does:

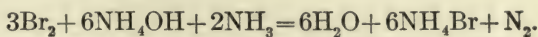
(a) In a cold dilute solution:



(b) On warming:



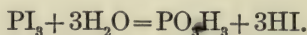
(c) Upon ammonia:



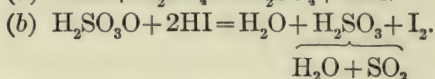
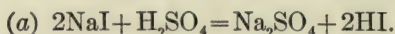
## HYDRIODIC ACID, HI.

*Occurrence.*—Iodine occurs in nature as the iodide and as the iodate;\* most frequently as the former, accompanying (in small amounts) chlorine and bromine; *e.g.*, in the ocean, in mineral waters, etc.

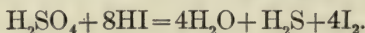
*Preparation.*—Hydriodic acid may be obtained pure by the action of an acid iodide upon water:



If we attempt to prepare hydriodic acid by the action of sulphuric acid upon iodides, even from dilute solutions, it is more difficult than in the case of hydrobromic acid to obtain a pure product, on account of the slight affinity that iodine has for hydrogen. The hydriodic acid thus obtained always contains a large amount of iodine, together with the reduction products of sulphuric acid; the latter varying in composition according to the concentration of the acid employed and of the iodide solution. Thus, with considerable concentrated sulphuric acid, sulphur dioxide is obtained:



But if, on the other hand, considerable hydriodic acid is present, the sulphuric acid is reduced down to hydrogen sulphide:



On heating considerable potassium iodide with concentrated sulphuric acid in a small test-tube, grayish, solid iodine separates out, which is volatile on warming, forming violet vapors. Furthermore, hydrogen sulphide is given off at the same time, as can be readily shown by the lead acetate paper test (see Hydrogen Sulphide).

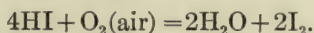
*Properties.*—Hydriodic acid is a colorless gas, with a suffocating odor; it fumes in moist air, and is readily soluble in water, forming a strongly-fuming liquid of sp. gr. 1.99–2.0. On account of the slight affinity which iodine possesses for hydrogen, an aqueous solu-

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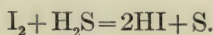
\* To the extent of 0.5 per cent. in Chili saltpeter.



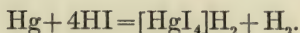
tion of hydriodic acid is even more difficult to keep than a solution of hydrobromic acid; it soon turns brown, owing to the separation of iodine:



If hydrogen sulphide is conducted into the brown solution, it is decolorized, with separation of sulphur:



On account of the instability of hydriodic acid, it attacks metals which are unaffected by both hydrochloric and hydrobromic acids; thus mercury is easily dissolved, with evolution of hydrogen:



Hydriodic acid (like hydrochloric and hydrobromic acids) is oxidized by peroxides, nitrates, nitrites, chromates, etc., with separation of iodine; only in this case the oxidation of the hydriodic acid takes place much more readily, so that a very dilute solution is oxidized by nitrous and chromic acids even in the cold. (See next pages.)

Hydriodic acid is a monobasic acid; its salts are called iodides.

The solubilities of the iodine compounds are almost exactly analogous to the corresponding bromine and chlorine compounds. Mercuric iodide,  $\text{HgI}_2$ , and palladium iodide,  $\text{PdI}_2$ , are, however, insoluble in water, while the corresponding chlorine and bromine compounds are soluble.

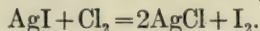
#### REACTIONS IN THE WET WAY.

1. **Dilute Sulphuric Acid** (1 : 10) attacks the iodides of the alkalis perceptibly, but only on warming.

2. **Concentrated Sulphuric Acid** reacts in the cold (cf. p. 294).

3. **Silver Nitrate** produces a yellow, curdy precipitate of silver iodide, insoluble in nitric acid, and only slightly soluble in ammonia,\* but readily soluble in potassium cyanide and sodium thiosulphate.

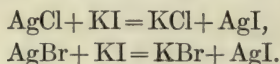
By the action of chlorine, silver iodide is readily changed into silver chloride:




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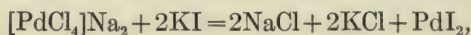
\* Treatment with ammonia causes the silver iodide to assume a much lighter color.

On the other hand, if chloride or bromide of silver is treated with potassium iodide it will be changed into silver iodide:



4. **Lead Salts** precipitate yellow lead iodide, soluble in considerable hot water and forming a colorless solution which deposits gold-yellow plates of  $\text{PbI}_2$  on cooling.

5. **Palladous Chloride** (it is best to use sodium palladous chloride) precipitates, from dilute solutions of an iodide, black palladous iodide (difference from chlorine and bromine).

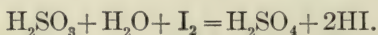


which is readily soluble in an excess of potassium iodide.

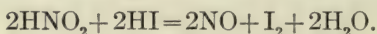
6. **Cupric Salts** are reduced by iodides, causing the separation of a brownish mixture of cuprous iodide and iodine:



If sulphurous acid is then added to the solution, a nearly white deposit of cuprous iodide is obtained, owing to the deposited iodine being changed to hydriodic acid by the sulphurous acid:



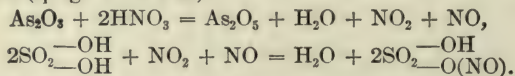
7. **Nitrous Acid.**—If a dilute solution of an iodide is treated with nitrous acid, iodine separates out and the solution becomes yellowish to brown in color (difference from chlorides and iodides):



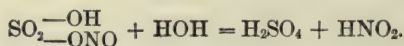
This extremely sensitive reaction is best performed as follows:

The solution to be tested is treated with a few drops of a solution of nitrous acid in concentrated sulphuric acid,\* a little carbon

\* This solution is prepared by heating arsenic trioxide with nitric acid (sp. gr. 1.30–1.35) and conducting the gases evolved ( $\text{NO}_2$  and  $\text{NO}$ ) into sulphuric acid (sp. gr. 1.75–1.80):

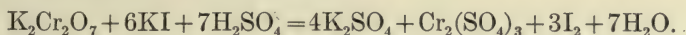


This solution of nitrosyl sulphuric acid is sometimes called “nitrose.” It can be kept for some time, but water decomposes it into nitrous and sulphuric acids:



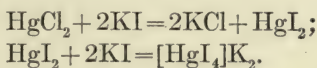
disulphide or chloroform is added and the mixture shaken, when the carbon disulphide (or the chloroform) becomes reddish-violet in color. The iodine set free may also be tested for with starch paste (see p. 299).

8. **Potassium Dichromate**, in the presence of dilute sulphuric acid, causes the separation of iodine from dilute iodide solutions in the cold; the iodine can be more easily recognized by shaking the solution with chloroform or carbon disulphide (difference from bromine):



By heating a mixture of solid iodide and solid potassium dichromate with concentrated sulphuric acid, iodine is set free (according to the above equation), which distils over, and can be condensed in the receiver. No chromium is carried over by this reaction (difference from chlorine).

9. **Mercuric Chloride** produces scarlet mercuric iodide, soluble in an excess of potassium iodide:

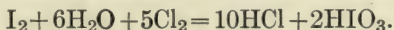


10. **Chlorine Water** sets free iodine from iodides,



which colors carbon disulphide reddish-violet, or starch-paste blue.

By adding an excess of chlorine water, the violet color disappears, the iodine being oxidized to colorless iodic acid:



#### Detection of Iodine in Non-electrolytes.

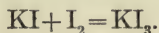
The processes to be employed are the same as those described for detecting chlorine in non-electrolytes (see page 284).

#### FREE IODINE.

Free iodine forms scales resembling graphite in appearance, and has a sp. gr. of 4.94 at 17° C. It melts at 114° C. (at the same temperature as sulphur), but begins to volatilize at ordinary temperatures, and is completely transformed into violet vapors at 200° C.



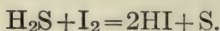
It is only slightly soluble in water (100 parts of water dissolve 0.02 parts of iodine), soluble to a considerable extent in alcohol and ether, forming a brown solution, and much more soluble in carbon disulphide and in chloroform; so that all the iodine from an aqueous solution can be removed by shaking a few times with either of these solvents. Iodine is still more soluble in hydriodic acid, or in a solution of an alkali iodide, forming a triiodide:



Commercial iodine always contains water, chlorine, bromine, and often cyanogen (iodine cyanide) as impurities.

An aqueous solution of iodine is a weak oxidizing agent.

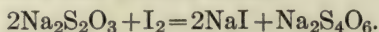
If hydrogen sulphide is passed through an aqueous solution of iodine, it becomes colorless and turbid, owing to the separation of sulphur:



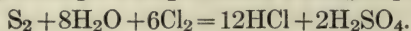
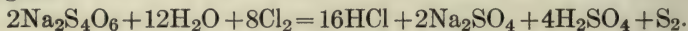
Solid iodine is not acted upon at ordinary temperatures by hydrogen sulphide; heat is necessary to produce the endothermic hydriodic acid.

In aqueous solution the necessary heat energy is furnished by the solution of the hydriodic acid formed in water. The fact that solid iodine is not acted upon by hydrogen sulphide, while it decomposes arsine, is utilized in the preparation of hydrogen sulphide free from arsenic from pyrites containing arsenic (cf. p. 221). The mixture of hydrogen sulphide and arseniuretted hydrogen is passed over iodine, and the latter only is removed.

**Sodium Thiosulphate** decolorizes iodine solutions, forming sodium tetrathionate and sodium iodide:

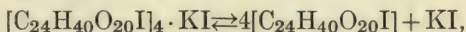


Chlorine and bromine react in exactly the same way upon sodium thiosulphate when they are not present in excess. In the latter case the reaction goes further and the tetrathionate is oxidized to sulphate and sulphuric acid with deposition of sulphur, and the sulphur itself is gradually oxidized to sulphuric acid by the halogens:



Other weak oxidizing agents, such as ferric and cupric salts, act upon thiosulphate similar to iodine (see Thiosulphuric acid).

**Starch Paste.**—Free iodine colors starch paste blue, but only in the presence of hydriodic acid or a soluble iodide. Opinions differ concerning the composition of "iodide of starch." Some hold that it is a compound, while others regard it as a solid solution.\* According to Mylius,† iodide of starch is the hydriodic acid compound of an iodine addition-product of starch, containing about 18 per cent iodine, corresponding to the formula  $[C_{24}H_{40}O_{20}I]_4 \cdot HI$ . This compound acts as an acid. If iodide of starch is produced in a neutral solution, in the presence of iodides, a salt of the above acid is formed, of which Mylius isolated the barium salt. Iodide of starch, then, can be regarded as a double salt, similar to carnallite,  $MgCl_2 \cdot KCl$ . In dilute solutions it must be dissociated into its components, *e.g.*, the potassium salt



and if we assume that the compound  $C_{24}H_{40}O_{20}I$  is colorless, the aqueous solution of starch iodide will be colorless; but on increasing the concentration of the alkali iodide, the double salt will be less dissociated and the blue color of the undissociated compound will appear, which corresponds with the facts. If a dilute aqueous iodine solution (obtained by shaking iodine with water) is added drop by drop to a dilute aqueous starch solution, a blue color will appear at the spot where the two solutions first come in contact, but this color will disappear on stirring. If some potassium (or other) iodide is added to the colorless solution of the starch and iodine, a permanent blue coloration will at once appear.‡

The temporary appearance of the blue color, immediately on adding the iodine solution, is probably due to the fact that the iodine first forms a substitution product with the starch, setting free hydriodic acid, which furnishes the conditions for the formation of the iodide of starch.

The fact that a starch solution containing an iodide is much more sensitive than one in pure water has been known for a long time.

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\* Küster, Ann. 283, 689 (1894), C. O. Harz, Chem. Zentr. 1898, I, 1018  
Andrews and Götsch, J. Am. Chem. Soc. 24, 865 (1906); Padra and Savori;  
Chem. Zentrabl., 1905, I, 1593; Katayama, Z. anorg. Chem. 56, 209 (1907).

† Mylius, Ber. 20, 688, and C. Lonnes, Z. anal. Chem. 33, 409.

‡ The blue color disappears on heating the solution, but reappears on cooling.

### Detection of Hydrochloric, Hydrobromic, and Hydriodic Acids in the Presence of One Another.

The solution to be tested should contain the alkali salts of the above acids. Half of this solution is taken for the bromide and iodide test, while the other half is retained for the chloride test.

#### (a) *Detection of Bromine and Iodine.*

1. The solution is acidified with dilute sulphuric acid, about one c.c. of colorless carbon disulphide, or chloroform, and a drop of chlorine water are added, and the mixture is shaken. If iodine is present (even in the presence of bromine), the carbon disulphide will be colored reddish-violet.

In order to detect the bromine, more chlorine water is added, with repeated shaking of the liquid, until the reddish-violet color has disappeared, showing that the iodine has been completely oxidized to iodic acid; the brown color of the bromine dissolved in the carbon disulphide will then appear and become a pale yellow on further addition of chlorine water.

2. Instead of using chlorine water, it is often better to test for iodine (especially when only small amounts are present, as in mineral waters) with nitrous acid. The solution to be tested for iodine and bromine is acidified slightly with dilute sulphuric acid, carbon disulphide and a few drops of a solution of nitrous acid in sulphuric acid are added, and the mixture shaken. If the carbon disulphide is colored reddish-violet, iodine is present. The aqueous solution is now poured off from the carbon disulphide (through a moistened filter, in order to remove any suspended drops of colored carbon disulphide), chlorine water is added, and the solution shaken with fresh carbon disulphide. If the latter now assumes a brown color, bromine is present.

#### (b) *Detection of Chlorine.*

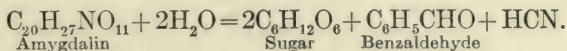
The simplest and surest way of separating chlorine from bromine and iodine is by fractional precipitation with silver nitrate. If the solution containing salts of the three halogens is treated with dilute silver nitrate, drop by drop, the iodine will be first precipitated as yellow silver iodide, then the bromide as a pale yellow



silver salt, and finally the chlorine as pure white silver chloride. To separate the chlorine from the other two halogens, a few drops of the solution to be tested are taken and acidified with nitric acid. A drop of silver nitrate (1 : 100) is added, and the mixture shaken and boiled, which causes the precipitate to collect together. If bromine or iodine is present, the precipitate is yellow. The precipitate is filtered off and again treated with the dilute silver nitrate, etc., until a pure white \* precipitate of silver chloride is obtained, in case chlorine is present.

### HYDROCYANIC ACID (PRUSSIC ACID), HCN.

*Occurrence.*—The compound of hydrogen with the univalent radical  $\text{—C}\equiv\text{N}$ , cyanogen seldom occurs in nature. It is found in all parts of a tree growing in Java (*Pangium Edule*), particularly in the seed kernels. Its compounds are found in many plants as a glucoside (amygdalin), which yields, on hydrolysis, sugar, benzaldehyde, and prussic acid:

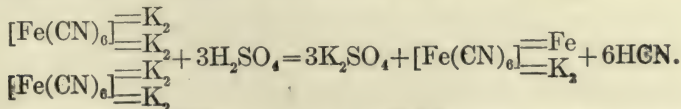


This amygdalin is found in bitter almonds, in the fruit kernels of cherries, apricots, peaches, etc., and in the leaves of the common laurel tree (*Prunus Laurocerasus*).

Amygdalin is usually accompanied by a ferment, so that, on macerating the parts of the plant which contain the amygdalin, an aqueous solution of prussic acid is obtained (bitter-almond water).

*Preparation.*—If ammonia is passed over glowing carbon, ammonium cyanide is formed; so that this salt, as well as other cyanogen compounds, is found in the "gas-water" obtained by the dry distillation of coal.

Hydrocyanic acid may also be prepared by adding acid to many cyanogen compounds. If yellow prussiate of potash is treated with dilute sulphuric acid and distilled, prussic acid is evolved, which, after standing over solid calcium chloride, may be obtained in the anhydrous condition as a colorless, exceedingly poisonous liquid, smelling of bitter almonds, and boiling at  $26.5^\circ \text{C}$ . :



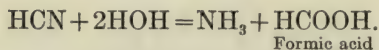

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\* By filtering off the precipitate it is easy to tell whether it is pure white, for the slightest tinge of yellow will show against the white paper.

The best method for preparing anhydrous hydrogen cyanide \* consists in allowing a mixture of equal volumes sulphuric acid and water to drop upon sticks of 98 per cent potassium cyanide. Hydrogen cyanide is evolved, contaminated with traces of water which can be removed by allowing the liquid to stand over solid calcium chloride.

*Properties.*—The liquid (as well as the gaseous) hydrocyanic acid burns with a reddish flame, and mixes in all proportions with water, alcohol, and ether.

Aqueous hydrocyanic acid cannot be kept indefinitely; a brown deposit soon appears, with the formation of formic acid and ammonia:

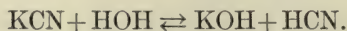


If a little mineral acid is added to the aqueous solution, it may be kept much longer; but, even then, ammonia and formic acid will be formed after a long time. Cold concentrated hydrochloric acid converts hydrocyanic acid into formamide,  $\text{HCN} + \text{H}_2\text{O} = \text{HCONH}_2$ , but on warming this compound is decomposed into carbon monoxide and ammonia.

Hydrocyanic acid in aqueous solution is a very poor conductor of electricity; in other words, it is a weak acid, and only dissociated to a slight extent.

The salts of hydrocyanic acid, the cyanides, are very similar in their properties to the corresponding halogen compounds, but are distinguished by their ability to form stable complex salts, which contain scarcely any cyanogen ions in aqueous solution, and consequently do not give some of the reactions for hydrocyanic acid.

*Solubility of Cyanides.*—The cyanides of the alkalis and alkaline earths are readily soluble in water, but are hydrolytically decomposed into metallic hydroxide and hydrocyanic acid, and their ions:



But as hydrocyanic acid is only slightly dissociated, the aqueous solution of an alkali cyanide behaves like a solution of alkali hydroxide containing free prussic acid; the smell of the latter can be readily detected.

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\* J. Wade and L. Panting, Proc. Chem. Soc. No. 190, p. 49 (1897-8).

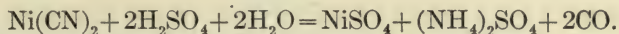
The remaining cyanides, with the exception of mercuric cyanide, are insoluble in water.

#### REACTIONS IN THE WET WAY.

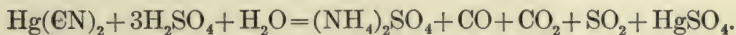
1. **Dilute Sulphuric Acid** decomposes solutions of all soluble cyanides, with the exception of mercuric cyanide, setting free hydrocyanic acid in the cold (recognizable by its odor).

The insoluble cyanides are decomposed by dilute sulphuric acid only on warming.

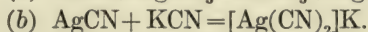
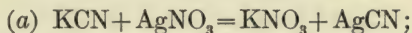
2. **Concentrated Sulphuric Acid** decomposes all cyanides on warming, the complex cyanides as well as the simple ones. The metals are then obtained in the form of sulphates, the carbon of the cyanogen is changed to carbon monoxide, and the nitrogen into ammonium sulphate:



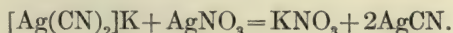
With mercuric cyanide, besides carbon monoxide, sulphur dioxide and carbon dioxide are obtained; for mercuric cyanide is decomposed at the temperature of boiling sulphuric acid into mercury and cyanogen; and the former dissolves in the hot sulphuric acid, with formation of mercuric sulphate and evolution of sulphur dioxide:



3. **Silver Nitrate.**—If silver nitrate is added to a solution of an alkali cyanide drop by drop, a precipitate is formed on the addition of each drop, which, however, redissolves on stirring the liquid, for silver cyanide is soluble in an excess of alkali cyanide:



The complex salt, silver potassium cyanide, is decomposed by further addition of silver nitrate, being finally completely transformed into insoluble silver cyanide:



Consequently the precipitation is only complete when an excess of silver nitrate is added.



Silver cyanide is insoluble in water and dilute nitric acid, perceptibly soluble in concentrated nitric acid, and readily soluble in ammonia, sodium thiosulphate, and potassium cyanide. Dilute nitric acid reprecipitates silver cyanide from the solution in ammonia or potassium cyanide.

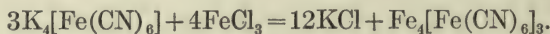
Concentrated hydrochloric acid decomposes silver cyanide, on warming, into silver chloride, with evolution of hydrocyanic acid (difference from silver chloride, bromide, or iodide).

By igniting silver cyanide, cyanogen gas is obtained, with metallic silver, and brown, difficultly-volatile paracyanogen, which, on further heating, is completely volatilized, leaving behind pure silver:

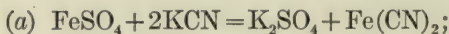


Much more certain than the silver nitrate test are the tests for hydrocyanic acid which depend upon the formation of Prussian blue or of ferric sulphocyanate.

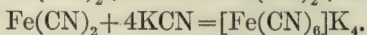
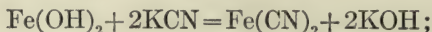
**4. Prussian Blue Reaction.**—Prussian blue is formed by the action of ferric salts upon potassium ferrocyanide (cf. p. 120).



In order, therefore, to apply this reaction to potassium cyanide, etc., it is necessary first to transform the cyanide into potassium ferrocyanide. This may be accomplished by the addition of a ferrous salt, whereby ferrous cyanide is first formed, which dissolves in an excess of potassium cyanide, forming potassium ferrocyanide:



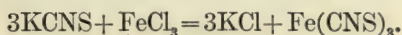
Potassium ferrocyanide is formed even more readily by the action of potassium cyanide upon ferrous hydroxide:



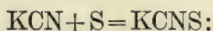
Evidently for the formation of the potassium ferrocyanide a little iron and considerable potassium cyanide are required. Consequently, to bring about the reaction, a little ferrous sulphate is added to the alkaline solution of an alkali cyanide, and the mix-

ture boiled. A little hydrochloric acid is then added, whereby a clear solution is obtained, which gives, with a little ferric chloride, the blue precipitate. If only traces of hydrocyanic acid were present, the solution appears green at first, but, after standing some time, "flocks" of Prussian blue will be precipitated.

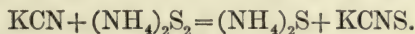
**5. The Ferric Sulphocyanate Reaction.**—Potassium sulphocyanate produces a red coloration with a ferric salt, owing to the formation of soluble ferric sulphocyanate (cf. p. 119):



The cyanide, therefore, must be changed to sulphocyanate in order to apply this reaction, which can be done by heating with sulphur:



or, better, by treatment with an alkaline polysulphide;



To the concentrated solution of the cyanide (in a porcelain dish) a little yellow ammonium sulphide is added, and the mixture evaporated on the water-bath to dryness. The residue is acidified with a little hydrochloric acid,\* and a drop of ferric chloride is added, whereby the characteristic blood-red coloration will be produced if only traces of cyanide are present.

**6. Mercurous Nitrate** produces a gray precipitate of metallic mercury when added to a solution of an alkali cyanide (difference from a chloride, bromide, or iodide):



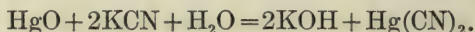
### Behavior of Mercuric Cyanide.

Mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , is a non-electrolyte, is quite soluble in water, in alcohol and in ether, and behaves quite differently from all other cyanides. All the above-mentioned reactions, with the exception of the ferric sulphocyanate test, fail with this compound. Mercuric cyanide solution gives no precipitate with silver nitrate, but a readily soluble double salt is

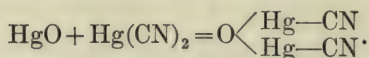
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\* It is necessary to acidify in order to destroy the  $(\text{NH}_4)_2\text{S}$ , which would precipitate black  $\text{Fe}_2\text{S}_3$  with  $\text{FeCl}_3$  and the red coloration would not appear.

formed,  $\text{Hg}(\text{CN})_2 \cdot \text{AgNO}_3 \cdot 2\text{H}_2\text{O}$ . Similarly there is no precipitate formed with ammonia, potassium iodide, alkali hydroxide, or alkali carbonate because all these reagents give, under ordinary conditions, precipitates of mercuric compounds which are soluble in potassium cyanide. Thus, for example, mercuric oxide dissolves easily in potassium cyanide:



Mercuric oxide itself is fairly soluble in mercuric cyanide:

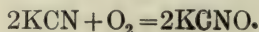


Hydrochloric, hydrobromic and hydriodic acid decompose mercuric cyanide readily, but it is scarcely attacked by dilute sulphuric acid alone. In the presence of a soluble chloride, however, mercuric cyanide is decomposed easily by sulphuric acid, or even by oxalic acid or tartaric acid. If, therefore, a solution of mercuric cyanide is treated with common salt and dilute sulphuric, oxalic or tartaric acid, then on subjecting the mixture to distillation, a distillate is obtained containing hydrocyanic acid, showing all the tests characteristic of this acid.

Mercuric cyanide in solution is acted upon by hydrogen sulphide or by alkali sulphides, forming mercuric sulphide and hydrocyanic acid, or one of its salts. If the black precipitate is removed by filtration, the ferric sulphocyanate test is obtained without difficulty.

### Behavior of Cyanides on Ignition.

The cyanides of the alkalis and alkaline earths fuse without decomposition when heated out of contact with the air; heated in contact with air, they absorb oxygen with avidity, forming a cyanate:

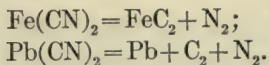


Consequently the alkali cyanides are strong reducing agents (cf. p. 255).

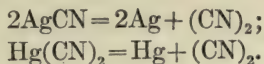
The cyanides of the bivalent heavy metals are decomposed on ignition, out of contact with the air into nitrogen and metallic car-



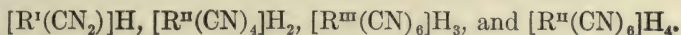
bide; the latter often being further decomposed into metal and carbon:



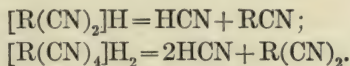
The cyanides of the trivalent metals are unknown in the free state; those of the noble metals are decomposed, by igniting, into metal and dicyanogen:



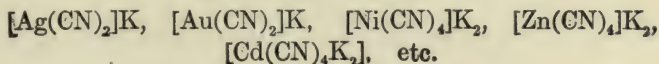
It is a characteristic property of the cyanides of the heavy metals that they are readily soluble in alkali cyanide solutions, forming very stable complex compounds, which are to be regarded as salts of the following acids:



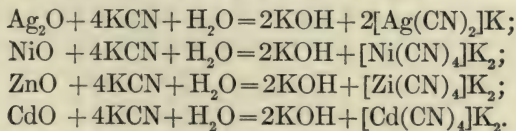
The first two of the above acids are so unstable that they are decomposed, as soon as they are set free, into hydrocyanic acid and cyanide:



Consequently all cyanides which are derived from these acids evolve hydrocyanic acid when treated with dilute hydrochloric or sulphuric acid in the cold. Such compounds are:



These salts must be regarded as complex compounds, for their aqueous solutions contain almost no heavy metal ions; they are not precipitated by caustic alkali, alkali carbonate, or ammonia. From this fact it follows that the oxides of these metals are soluble in cyanides of the alkalies, forming the following complex salts;



Hydrogen sulphide decomposes the silver and cadmium salts

without difficulty the zinc salt slightly, and the nickel salt not at all.

The acids of the general formula  $[R^{III}(CN)_6]H_3$  and  $[R^{II}(CN)_6]H_4$  are, in contrast with the above acids, quite stable in the free state, and can be usually obtained, without the evolution of hydrocyanic acid, by acidifying a solution of one of their salts with cold dilute mineral acid; but, on warming the acid solution, hydrocyanic acid is given off.

As typical representatives of these acids we have hydroferri- and hydroferrocyanic acids, and hydrocobalticyanic acid.\*

We will consider hydroferro- and hydroferri- cyanic acids separately; but before doing so we will briefly describe

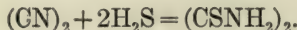
#### DICYANOGEN,

which is obtained by heating the cyanides of the noble metals, as a colorless gas with a disagreeable odor; it burns with a reddish flame, and is soluble in water (25 parts water dissolve 100 parts of dicyanogen). The aqueous solution cannot be kept very long, as brownish "flocks" separate out little by little (azulmic acid,  $C_4H_5N_5O$ ) and the solution then contains ammonium cyanide, ammonium carbonate, ammonium oxalate, and urea.

Just as chlorine acts upon caustic alkalis, forming chloride and hypochlorite, so dicyanogen reacts with them, forming a cyanide and a cyanate:



On conducting hydrogen sulphide into a solution of dicyanogen, a red, crystalline precipitate of hydrorubianic acid is obtained



Cf. page 201.

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\*Hydrocobaltocyanic acid is extremely unstable, like hydromangano- and hydromanganicyanic acids. Their salts evolve HCN when treated with cold, dilute, mineral acids.

**Detection of Nitrogen in Organic Substances. (Lassaigne.)**

If a little nitrogenous, organic substance is placed with some metallic sodium in a small glass tube closed at one end, and heated till the glass begins to soften, then the nitrogen and some of the carbon of the organic substance will combine with the sodium to form sodium cyanide. After heating for two minutes, the hot end of the glass tube is placed in a little water, whereby the glass breaks and the contents of the tube are immediately wet by water. The alkaline solution containing the sodium cyanide is filtered from residual carbon and glass splinters, a little ferrous sulphate solution is added; and then, after boiling, a few drops of ferric chloride solution are added and enough hydrochloric acid to neutralize the alkali. If nitrogen was present in the original substance, Prussian blue is now obtained.

*Remark.*—Certain nitrogenous substances are decomposed with evolution of nitrogen before the temperature required for the cyanide formation is reached \* and thus the nitrogen escapes the Lassaigne reaction; in other cases the experiment fails on account of the extreme volatility of the organic substance.†

According to E. A. Kehrre,‡ the Lassaigne reaction gives positive results in all cases if the sodium is first heated by itself and then brought in contact with the vapors of the organic material. The experiment is carried out in a small tube, drawn out at the closed end, such as used for the arsenic test (cf. Fig. 21, p. 223). The substance is placed in the restricted part of the tube and then, in the wider part, just before the restriction is reached, a small piece of sodium is introduced which has been rolled between the fingers and freed from petroleum by touching it to filter paper. The sodium is heated until it glows and then, by means of another, small flame, the substance to be tested is heated so that it melts and the vapors just rise up to the glowing sodium but hardly reach through it. By taking away the small flame, the vapors can be made to condense and be driven toward the glowing sodium again. Otherwise, the test is carried out exactly as described above.

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\* Gräbe, Ber. **17**, 1178 (1884).

† Feist, Ber. **35**, 1559 (1902).

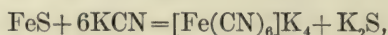
‡ Ber. **35**, 2523 (1902).



**HYDROFERROCYANIC ACID**  $[\text{Fe}''(\text{CN})_6]\text{H}_4$ .

Hydroferrocyanic acid is a white, solid substance, which is readily soluble in water and in alcohol, the solution soon becoming blue on exposure to air. The salts of this acid are much more stable than the acid itself, being all prepared from the potassium salt, the yellow prussiate of potash. This potassium salt, the most important ferrocyanide of commerce, is obtained by the fusion of organic substances containing nitrogen and sulphur (blood, etc.) with potash and metallic iron, and by lixiviating the product of the fusion with water.

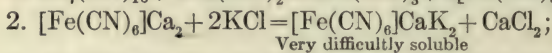
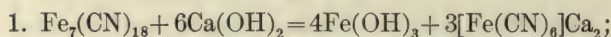
In the melt, iron sulphide and potassium cyanide are found, which, on treatment with water, are changed to potassium ferrocyanide and potassium sulphide,



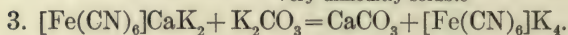
and, on evaporating the solution, the former salt separates out (with three molecules of water of crystallization) in the form of large, yellow, tetragonal octahedrons.

Recently this salt has been obtained as a by-product in the manufacture of illuminating-gas, Prussian blue and ammonium sulphocyanate being formed from the purification of the gas.

The following equations will give some idea of the formation of potassium ferrocyanide in the gas-house:



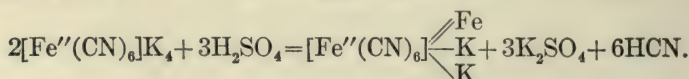
Very difficultly soluble



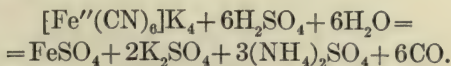
*Solubility of Ferrocyanides.*—The ferrocyanides of the alkalis and alkaline earths are soluble in water; but the remaining salts dissolve with difficulty (if at all) in water and in cold dilute acids.

**REACTIONS IN THE WET WAY.**

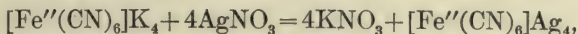
**1. Dilute Sulphuric Acid.**—The ferrocyanides are not decomposed by cold dilute sulphuric acid, but break up at the boiling temperature with evolution of hydrocyanic acid:



2. **Concentrated Sulphuric Acid** decomposes ferrocyanides completely, on warming, with evolution of carbon monoxide, which burns with a blue flame:\*



3. **Silver Nitrate** produces a white precipitate of silver ferrocyanide,



insoluble in dilute nitric acid and ammonia, but soluble in potassium cyanide solution. On treatment with concentrated nitric acid, it is changed to orange silver ferricyanide, and is then soluble in ammonia.

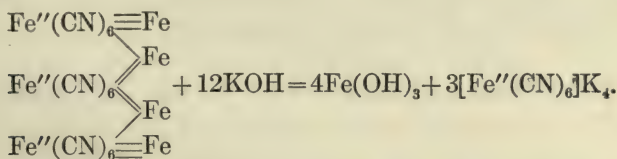
4. **Barium Chloride** gives no precipitation.

5. **Ferric Salts** produce a precipitate of Prussian Blue in neutral or acid solutions (cf. page 120).

6. **Ferrous Salts** yield a light blue precipitation, which changes to a darker blue on exposure to the air (cf. page 114).

7. **Cupric and Uranyl Salts** produce brown precipitates.

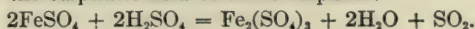
In order to detect ferrocyanic acid in an insoluble ferrocyanide, the latter is boiled with caustic soda or potash, when insoluble metallic hydroxide and an alkali ferrocyanide are usually formed. Thus, Prussian blue yields ferric hydroxide and potassium ferrocyanide:



The insoluble hydroxide is filtered off, the filtrate is acidified with dilute hydrochloric acid and treated with ferric chloride, whereby Prussian blue is again formed.

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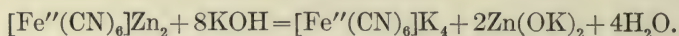
\*  $\text{SO}_2$  is also liberated by this reaction, as a part of the ferrous sulphate is oxidized by the sulphuric acid to ferric sulphate:



Prussian blue is often used in wall-papers as a pigment. If it is desired to detect the presence of this compound in a wall-paper, about 100 cm<sup>2</sup>. of the paper are cut into small pieces, boiled with caustic potash solution, filtered, and the filtrate treated according to the process just described. In a few hours a distinct blue precipitate of Prussian blue will be visible in the bottom of the test-tube, if originally present.

Some insoluble ferrocyanides do not yield the hydroxide of the metal on treatment with caustic alkali. Thus the brown uranyl ferrocyanide yields insoluble yellow potassium uranate and soluble potassium ferrocyanide (cf. page 128).

Insoluble zinc ferrocyanide is completely soluble in caustic alkali, forming an alkali zincate and soluble ferrocyanide:



In order to separate the zinc from the ferrocyanide, carbonic acid is conducted into the solution, the latter is boiled, and the insoluble zinc carbonate is filtered off. The filtrate then contains potassium ferrocyanide, which can be detected as above.

8. **Lead Salts** precipitate white lead ferrocyanide insoluble in dilute nitric acid.

#### Detection of Hydrocyanic Acid in the Presence of Hydroferrocyanic Acid.

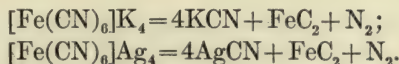
As the soluble ferrocyanides evolve no hydrocyanic acid on treatment with cold dilute hydrochloric acid, while the soluble cyanides do, it is evident that hydrocyanic acid can be detected in the presence of hydroferrocyanic acid. For this purpose, the mixture of the solid salts is placed in a small porcelain evaporating-dish, a little dilute hydrochloric acid is added, the dish is covered with another porcelain dish whose inner surface is wet with yellow ammonium sulphide, and the dishes are allowed to remain in this position for a few minutes.

The volatile hydrocyanic acid produces ammonium cyanate in the upper dish. The latter is acidified with hydrochloric acid, and a drop of ferric chloride is added. A blood-red coloration of ferric sulphocyanate shows the presence of hydrocyanic acid in the original compound.

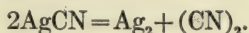


**Behavior of Ferrocyanides on Ignition.**

On being ignited, the ferrocyanides yield iron carbide, cyanide, and nitrogen:

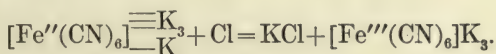


In the latter case, the silver cyanide is further decomposed into metal and dicyanogen:

**HYDROFERRICYANIC ACID,  $[\text{Fe}'''(\text{CN})_6]\text{H}_3$ .**

Hydroferricyanic acid forms brown needles, readily soluble in water.

Its salts, the ferricyanides, are very stable, and are obtained by the *oxidation* of the corresponding ferrocyanides. The most important of all these salts, potassium ferricyanide (red prussiate of potash),  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , is obtained by the oxidation of potassium ferrocyanide with chlorine:



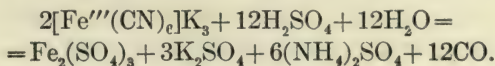
Bromine, hydrogen peroxide, etc., may be used instead of chlorine.

*Solubility of Ferricyanides.*—The ferricyanides of the alkalies and alkaline earths, and the ferric salt of hydroferricyanic acid, are soluble in water, but the remaining salts are insoluble even in dilute acids.

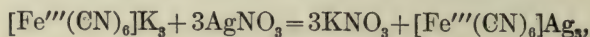
**REACTIONS IN THE WET WAY.**

1. **Dilute Sulphuric Acid** evolves no hydrocyanic acid in the cold (difference from cyanides), but does so on warming with the acid.

2. **Concentrated Sulphuric Acid** decomposes all ferricyanides, on warming, with the formation of sulphates and carbon monoxide:



3. **Silver Nitrate** produces orange silver ferricyanide:



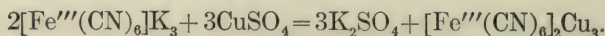
soluble in ammonia, but insoluble in nitric acid.

4. **Barium Chloride** gives no precipitation.

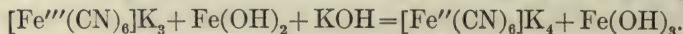
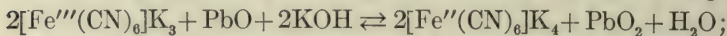
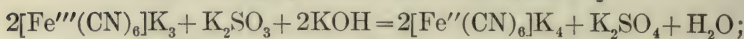
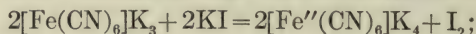
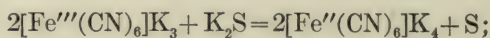
5. **Ferrous Salts** produce, in neutral and acid solutions, a precipitate of Turnbull's blue (cf. page 115).

6. **Ferric Salts** produce no precipitation, but a brown coloration.

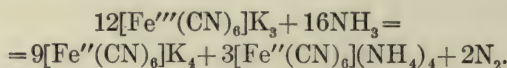
7. **Cupric Salts** yield green cupric ferricyanide:



8. **Behavior of the Ferricyanides in Alkaline Solutions.**—Hydroferricyanic acid is a strong oxidizing agent in alkaline solutions, being readily reduced to hydroferrocyanic acid by hydrogen sulphide, hydriodic acid, sulphurous acid, ferrous hydroxide, manganous hydroxide, lead oxide, starch, cellulose (paper), etc.; *e.g.*:



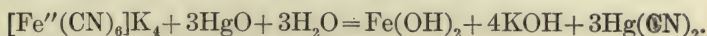
The ferricyanides are even reduced by ammonia, forming nitrogen:



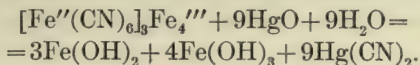
On account of this easy reducibility of hydroferricyanic acid, it is often difficult, sometimes impossible, to detect its presence, particularly in an insoluble compound. If Turnbull's blue is boiled with caustic potash, the residue will consist of a mixture of ferrous and ferric hydroxides, and the solution will contain potassium ferrocyanide. See p. 115.

The behavior of cyanides toward suspended yellow mercuric oxide is very important. Almost all cyanides, simple or complex, with the exception of potassium cobalticyanide, are completely

decomposed by this reagent. Mercuric cyanide and an oxide of the other metal are formed, which, if insoluble, may be separated from the mercuric cyanide by filtration. Thus potassium ferrocyanide is decomposed by mercuric oxide as follows:



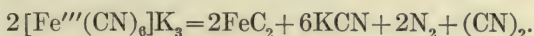
Prussian blue as follows:



This decomposition of the cyanides by mercuric oxide is often used in quantitative analysis for the separation of metallic cyanides.

#### Behavior of the Ferricyanides on Ignition.

The ferricyanides are decomposed into iron carbide, cyanide, dicyanogen, and nitrogen:

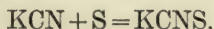


By heating a ferricyanide in a closed tube, dicyanogen therefore is given off, which burns with a reddish flame.

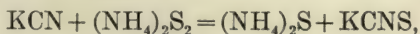
#### SULPHOCYANIC (THIOCYANIC) ACID, HCNS.

Thiocyanic acid is found in small amounts, in the form of its sodium salt, in saliva and urine.

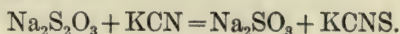
The free acid is a colorless, unstable liquid, with a penetrating odor. It can be kept better in aqueous solution than in the anhydrous state, but its salts, the sulphocyanates, are much more stable than the acid itself. The alkali salts can be prepared from the corresponding cyanides by heating with sulphur:



They may also be prepared by treating hydrocyanic acid or an alkali cyanide with an alkali polysulphide at ordinary temperatures:



or by boiling an alkali thiosulphate solution with an alkali cyanide (cf. page 379):





**Solubility.**—Most of the thiocyanates are soluble in water; exceptions are the silver, mercury, copper, and gold salts. Lead thiocyanate is difficultly soluble in water; and on boiling with water it is decomposed.

#### REACTIONS IN THE WET WAY.

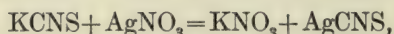
1. **Dilute Sulphuric Acid** (double normal) causes no reaction.

2. **Moderately Concentrated Sulphuric Acid** ( $5\text{H}_2\text{SO}_4:4\text{H}_2\text{O}$ ) decomposes the thiocyanates, with evolution of carbonyl sulphide, which burns with a blue flame:



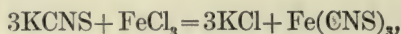
3. **Concentrated Sulphuric Acid** violently decomposes thiocyanates, with evolution of very disagreeably-smelling vapors, COS, HCOOH,  $\text{CO}_2$ ,  $\text{SO}_2$ , and deposition of sulphur.

4. **Silver Nitrate** precipitates white, curdy, silver sulphocyanate:



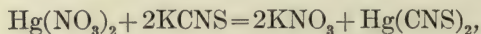
insoluble in dilute nitric acid, soluble in ammonia.

5. **Ferric Salts** produce a blood-red coloration, due to the formation of ferric sulphocyanate:



very soluble in ether (cf. page 119).

6. **Mercuric Nitrate** precipitates white mercuric thiocyanate:



very difficultly soluble in water, but readily soluble in an excess of potassium sulphocyanate:

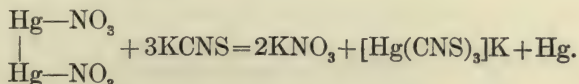


If the dry powder is heated, the salt expands greatly (Pharaoh's serpents).

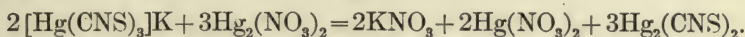
7. **Mercuric Chloride** gives a precipitate only after long standing.

8. **Mercurous Nitrate** produces a gray to black precipitate. On adding mercurous nitrate drop by drop to a fairly-concentrated

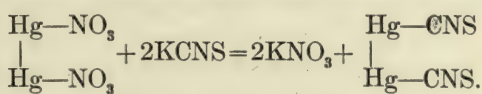
solution of potassium sulphocyanate, a gray precipitate of metallic mercury is first obtained, and the solution contains potassium mercuric sulphocyanate:



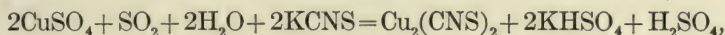
If the addition of mercurous nitrate is continued until no more mercury is precipitated, and the solution then filtered, the filtrate will contain mercuric potassium sulphocyanate; but, on adding still more mercurous nitrate, pure white, mercurous sulphocyanate is precipitated:



If, on the other hand, a very dilute solution of potassium sulphocyanate is added to a very dilute solution of mercurous nitrate, the white precipitate of mercurous sulphocyanate is obtained directly:



**9. Cupric Salts.**—On adding a few drops of a solution containing a cupric salt to one of an alkali sulphocyanate, the solution is colored emerald-green; and, on further addition of the copper solution, black cupric sulphocyanate is precipitated. If sulphurous acid is added, white cuprous sulphocyanate is deposited,



insoluble in dilute hydrochloric and sulphuric acids.

**10. Cobalt Salts.**—If a solution containing an alkali sulphocyanate is treated with a small amount of a cobalt salt, and the solution shaken with a mixture of equal parts amyl alcohol and ether,\* the upper layer of alcohol ether separates out azure-blue in color (cf. page 159). This reaction is analogous to that of cyanic acid upon cobalt salts (cf. page 334).

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\* Or with amyl alcohol alone.

### Detection of Ferrocyanides, Ferricyanides, and Thiocyanates in the Presence of One Another.\*

The dilute solution of the alkali salts of these acids is made slightly acid with acetic or hydrochloric acid and a solution of thorium nitrate is added, whereby thorium ferrocyanide is precipitated. To aid in filtration, the liquid is shaken with finely-divided asbestos, then filtered and washed with cold water. By pouring dilute caustic soda solution through the filter, acidifying the resulting solution with hydrochloric acid, and adding ferric chloride solution, the presence of ferrocyanic acid is confirmed by a precipitate of Prussian blue.

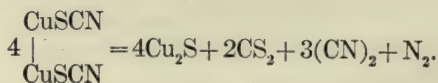
The filtrate from the thorium ferrocyanide is treated with cadmium sulphate, the solution shaken with asbestos, and the cadmium ferricyanide filtered, washed with cold water and dissolved in caustic soda. After acidifying this last solution with hydrochloric acid and adding ferrous sulphate, the presence of ferrocyanic acid is proved by the formation of Turnbull's blue.

The filtrate from the cadmium ferricyanide precipitate yields, upon the addition of ferric chloride solution, the blood-red color of ferric thiocyanate.

### Behavior of Thiocyanates on Ignition.

The thiocyanates of the alkalies melt readily, and are colored successively yellow, brown, green, and finally blue, becoming white again on cooling.

The thiocyanates of the heavy metals are decomposed into sulphide, splitting off carbon disulphide, dicyanogen, and nitrogen. Thus cuprous thiocyanate is decomposed according to the following equation:



The mercuric thiocyanates swell tremendously on being heated (Pharaoh's serpents).

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\* P. E. Browning and H. E. Palmer, *Z. anorg. Chem.*, **54**, 315 (1907).



## GROUP II.

**Silver Nitrate** produces a precipitate soluble in nitric acid.

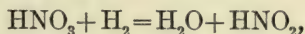
**Barium Chloride** causes no precipitation.

NITROUS ACID ( $\text{HNO}_2$ ).

*Occurrence.*—Nitrous acid never occurs free in nature except in the form of its salts, the nitrites. It is found in the air, as ammonium nitrite, in many soils and waters, particularly in those which are contaminated with ammonia or decaying substances.

Ammonia is oxidized by the action of micro-organisms (*monas nitrificans*) to nitrous acid, which combines with more ammonia to form ammonium nitrite.

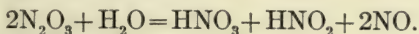
*Preparation of Nitrous Acid and its Salts.*—Nitrous acid is formed by the gentle reduction of nitric acid. If zinc is allowed to act upon dilute nitric acid for a short time, the latter is reduced to nitrous acid,



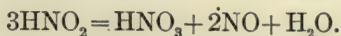
but the reduction can easily go a little farther, forming  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{N}_2$ ; while by long-continued action of the zinc, hydroxyl amine,  $\text{NH}_2\text{OH}$ , and ammonia even, are formed.

If nitric acid of sp. gr. 1.3 is heated with arsenious acid, starch etc., a mixture of nitric oxide and nitrogen peroxide is obtained, which, on cooling to  $-21^\circ \text{C}$ ., condenses to a bluish-green liquid,  $\text{N}_2\text{O}_3$ , the anhydride of nitrous acid.

If the anhydride is treated with ice-cold water, a bluish-green liquid is obtained, which contains nitrous acid, but always in company with nitric acid; for  $\text{N}_2\text{O}_3$  unites with water, forming nitrous and nitric acids, and nitric oxide:



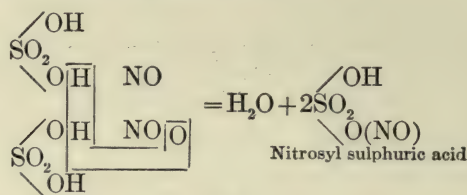
At a higher temperature nitrous acid is gradually changed into nitric acid:



Pure nitrous acid, therefore, is not known.

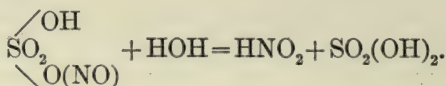
If the above mixture of nitric oxide and nitrogen peroxide is con-

ducted into concentrated sulphuric acid, the two gases are readily absorbed, forming nitrosyl sulphuric acid:



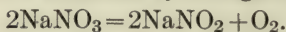
This solution of nitrosyl sulphuric acid in sulphuric acid is sometimes called "nitrose."

If this solution is added to cold water, sulphuric and nitrous acids are formed:



This solution of nitrosyl sulphuric acid can be kept indefinitely, so that it is a convenient reagent for the immediate production of nitrous acid at any time.

The salts of nitrous acid, the nitrites, are much more stable than the free acid, and may be obtained by the ignition of nitrates:



Nitrites prepared in this way always contain some oxide and some nitrate as impurity.\* In order to obtain a pure nitrite, silver nitrite is treated with a calculated amount of a metallic chloride:



The soluble nitrite can be separated from the insoluble silver chloride by filtration.

*Solubility of Nitrites.*—All nitrites are soluble in water; but silver nitrite and potassium cobaltic nitrite are difficultly soluble.

#### REACTIONS IN THE WET WAY.

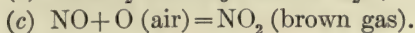
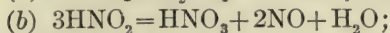
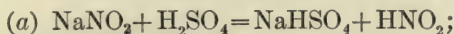
As all nitrites are soluble in water, the reactions which serve for their detection cannot be those of precipitation, but rather those in

\* If the nitrate is heated with a metal, e.g., lead, the reduction takes place at a lower temperature and is almost quantitative.

which a change of color takes place, owing to an oxidation or a reduction.

Nitrous acid sometimes acts as an oxidizing agent, and sometimes as a reducing agent.

1. **Dilute Sulphuric Acid** decomposes all nitrites in the cold, setting free brown vapors:



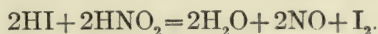
2. **Concentrated Sulphuric Acid** reacts exactly the same, but much more violently.

3. **Silver Nitrate** precipitates from nitrite solutions crystals of silver nitrite in the form of needles, which are very difficultly soluble in cold water (300 parts of water dissolve one part of silver nitrite at the ordinary temperature). In boiling water, silver nitrite is considerably more soluble.

4. **Cobalt Salts** produce (with an excess of potassium nitrite and acetic acid) a yellow crystalline precipitate of potassium cobaltic nitrite (cf. page 158).

5. **Indigo Solution** is completely decolorized by warming with nitrous acid.

6. **Hydriodic Acid** is oxidized by nitrous acid with separation of iodine:



If, therefore, a nitrite is added to a solution of potassium iodide, and the solution acidified with sulphuric or acetic acid,\* the solution becomes yellow, owing to the separation of iodine. If the solution is now shaken with chloroform or carbon disulphide, the

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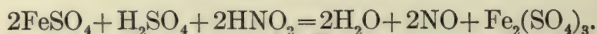
\* In the presence of considerable alkali acetate, there is no separation of iodine on the addition of acetic acid; but there is on the addition of a drop of a stronger acid. This is a beautiful illustration of the "Law of Mass Action." The dissociation of the acetic acid is lessened by the presence of the alkali acetate (or ammonium acetate), so that not enough H ions are present to decompose the nitrite, although enough are present to redden litmus distinctly. (Private communication from E. Bamberger.)



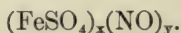
latter will be colored reddish-violet. Or if a little starch paste is added, it will be colored blue by the iodine.

This exceedingly delicate reaction is also caused by the action of a great many other oxidizing agents; and it can only be used for the detection of nitrous acid when it is known that all such oxidizing substances are absent.

**7. Ferrous Salts** are oxidized to ferric salts, with evolution of nitric oxide:



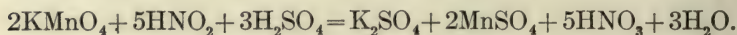
The nitric oxide dissolves, in the cold, in the excess of ferrous salt, forming a brown compound of a varying composition:



To perform this reaction a concentrated solution of ferrous sulphate is taken, slightly acidified, and the solution to be tested carefully poured on top. At the zone of contact between the two solutions the dark-brown coloration will be apparent.

Nitric acid gives the same reaction, but only on the addition of concentrated sulphuric acid.

**8. Potassium Permanganate.**—If nitrous acid is added to a warm acid solution (about 40° C.) of potassium permanganate, the latter will become decolorized, owing to the oxidation of the former to nitric acid:



In this reaction nitrous acid acts as a reducing agent.

**9. Detection of Small Amounts of Nitrous Acid by the Peter Griess Method.\***—As was already mentioned, nitrous acid is often found in drinking-water, in consequence of the oxidation of ammonia which results from the decay of organic substances (urine, etc.)

In order to detect the small amounts of nitrous acid which may be present in drinking-water, of the above reactions only that of potassium iodide and starch is delicate enough. But as hydrogen peroxide and ferric salts are also likely to be present, both of which cause the separation of iodine from an acid solution of potassium

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\* Ber. 12, 427 (1879).

iodide, it is evident that dependence upon this reaction alone would often lead to error.

Consequently, in order to detect the presence of traces of nitrous acid we make use of a reaction which was first proposed by Peter Griess, and which is caused by nitrous acid only. It depends upon the formation of an intensely-colored azo dyestuff.

Peter Griess used as his reagent phenylene diamine, whereby a yellow dye, Bismarck brown, is formed. Recently, according to the suggestion of Ilosvay v. Ilosva,\* an acetic acid solution of sulphanilic acid and of  $\alpha$ -naphthylamine is used instead. According to Lunge,† it is best to mix the solutions of the last two reagents.

The reagent is prepared as follows:

1. 0.5 gm. of sulphanilic acid is dissolved in 150 c.c. of dilute acetic acid.

2. 0.2 gm. of solid  $\alpha$ -naphthylamine is boiled with 20 c.c. of water, the colorless solution is poured off from the bluish-violet residue, and 150 c.c. of dilute acetic acid are added to it.

The two solutions are then mixed and can be kept for a long time, provided the mixture is not brought in contact with free nitrous acid. If the solution should become reddish, it can be decolorized by shaking with zinc dust and filtering.

*Procedure.*—About 50 c.c. of the water to be tested are treated with 2 c.c. of the above reagent. The liquid is well stirred and allowed to stand five to ten minutes, when it will be colored a distinct red if the slightest traces of nitrous acid are present.

10. **Diphenylamine**, dissolved in concentrated sulphuric acid, is colored intensely blue by nitrous acid. Nitric acid and many other oxidizing substances, such as selenic acid, chloric acid, ferric chloride, etc., will give the same reaction (cf. Nitric Acid).

11. **Brucine** dissolved in concentrated sulphuric acid (according to G. Lunge and A. Lwoff ‡) gives no reddish coloration when treated with nitrosyl sulphuric acid.

Dry, several times recrystallized, silver nitrite, containing 70.05 per cent. silver (theory 70.09), did give with brucine, (cf. page 384) in an atmosphere of carbon dioxide, a weak but

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\* Bull. chim. [3] 2, p. 317.

† Z. angew. Chemie, 1889, Heft 23.

‡ Z. angew. Chemie, 1894, 345.

nevertheless distinct test for nitric acid, probably due to the presence of traces of nitrate remaining in the silver nitrite. On dissolving 15 mgm. of this same nitrite in water, adding an equivalent amount of sodium chloride and diluting to one liter, a solution of sodium nitrite was obtained, of which one cubic centimeter added *drop by drop* with *constant stirring* to about four cubic centimeters of concentrated sulphuric acid yielded a solution of nitrosyl sulphuric acid, showing no sign of a red coloration with a drop of brucine reagent. The test was immediately obtained, however, on adding a trace of nitric acid to this solution.

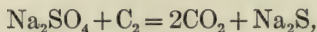
Brucine, therefore, is a reagent by which nitric acid can be detected in the presence of nitrous acid.

For a description of the behavior of nitrous acid toward ammonium salts and urea, see page 385.

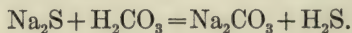
### HYDROSULPHURIC ACID (HYDROGEN SULPHIDE), $H_2S$ .

*Occurrence and Preparation.*—Hydrogen sulphide is found in volcanic regions, in many mineral waters (the so-called “sulphur” waters), and, in general, wherever substances containing sulphur are subject to decay, or when they come in contact with decaying substances. Sulphates are easily changed into sulphides by the action of micro-organisms which are present in the air; and this is the reason why many mineral waters containing sulphates smell of hydrogen sulphide after standing some time in a corked flask. If, however, the flask and the cork are sterilized, the water can be kept indefinitely. The formation of hydrogen sulphide from sulphates takes place as follows:

By means of carbonaceous matter (dust, etc.) the sulphates are reduced with the aid of micro-organisms, at first to sulphides.



which are then decomposed by carbonic acid:



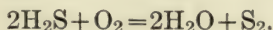
Just as hydrogen sulphide may be made from sodium sulphate by the action of organic matter in a corked flask, so



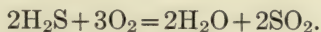
in nature the same process brings about the presence of hydrogen sulphide in many mineral waters.

For laboratory purposes, hydrogen sulphide is similarly prepared by the action of dilute sulphuric or hydrochloric acid upon a sulphide (usually iron sulphide, on account of its cheapness and stability).

*Properties.*—Hydrogen sulphide is a colorless gas, with an odor like that of rotten eggs; it is absorbed by water at the ordinary temperatures (one volume water absorbs two to three times its own volume). The aqueous solution reacts slightly acid toward litmus (toward methyl orange it has almost no action), and becomes turbid on standing in the air, owing to its oxidation by atmospheric oxygen:

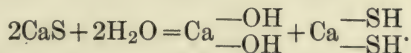


Hydrogen sulphide burns in the air with a bluish flame to water and sulphur dioxide:



The salts of hydrosulphuric acid are called sulphides.

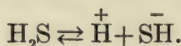
*Solubility of Sulphides.*—The sulphides of the alkalies and the hydro- and polysulphides of the alkaline earths are soluble in water. The monosulphides of the alkaline earths, particularly calcium sulphide,  $\text{CaS}$ , are very difficultly soluble in water, but they are gradually changed from contact with water into soluble hydrosulphides:



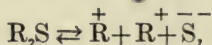
The remaining sulphides are insoluble in water. Of these latter  $\text{FeS}$ ,  $\text{MnS}$ , and  $\text{ZnS}$  are decomposed by dilute hydrochloric acid with evolution of hydrogen sulphide; others require concentrated hydrochloric acid, *e.g.*,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}_2$ ,  $\text{PbS}$ ,  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{CdS}$ ; while the remaining are insoluble in concentrated hydrochloric acid, but are all soluble in aqua regia with separation of sulphur.

## REACTIONS IN THE WET WAY.

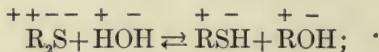
Free hydrogen sulphide, as has been stated, is a very weak acid, being even weaker than carbonic acid. In aqueous solution, therefore, it is very slightly dissociated into H and SH ions:



The soluble neutral salts  $\text{R}_2\text{S}$  are decomposed into metal and sulphur ions,



but under the influence of water, some of the bivalent sulphur ions go over into the univalent HS ions,

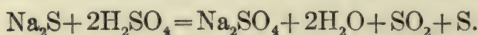


but some bivalent sulphur ions remain in solution, and, in fact, more in concentrated solutions than in dilute ones.

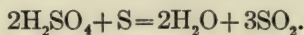
As, therefore, an aqueous solution of a sulphide contains both S ions and SH ions, while the solutions of the free acid only contain SH ions, it is plain why in many reactions the former react in a somewhat different way from the latter.

1. **Dilute Sulphuric Acid** decomposes all soluble, and some insoluble, sulphides, with evolution of hydrogen sulphide.

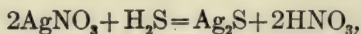
2. **Concentrated Sulphuric Acid** decomposes all sulphides, on warming, with evolution of sulphur dioxide and deposition of sulphur:



But even the sulphur goes over into sulphur dioxide after being heated with the sulphuric acid for some time:



3. **Silver Nitrate** produces, in solutions of hydrogen sulphide and of soluble sulphides, a black precipitate of silver sulphide,



insoluble in cold nitric acid, in which, however, it dissolves on warming.

4. **Barium Chloride** causes no precipitation.

5. **Lead Salts** (best a solution containing an excess of alkali) produce a black precipitate of lead sulphide. All sulphides which are decomposed by hydrochloric acid evolve hydrogen sulphide, which, on coming in contact with a piece of filter-paper moistened with an alkaline lead solution, colors the latter black. An insoluble sulphide (pyrite, arsenic sulphide, mercuric sulphide, etc.) evolves hydrogen sulphide with hydrochloric acid and nascent hydrogen. In this case some powdered zinc is placed in a small test-tube, a little of the insoluble sulphide added, then more zinc; the mixture is next warmed with concentrated hydrochloric acid and the evolved gas tested for hydrogen sulphide with lead paper. Traces of hydrogen sulphide can be detected with certainty by this reaction.

6. **Sodium Nitroprusside**,  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_2 + 2\text{H}_2\text{O}$ , is colored reddish-violet by S ions, but not by SH ions. Consequently hydrogen sulphide itself does not give this reaction, except upon the addition of caustic alkali. This reaction is very sensitive, but not so delicate as the one with an alkaline solution of a lead salt.

7. **Methylene Blue**.—This reaction (which is recommended by Emil Fisher\*) is the most sensitive of all reactions for detecting the presence of hydrogen sulphide. It is particularly suited for detecting the presence of traces of hydrogen sulphide in mineral waters, even when all other tests give negative results.

The solution to be tested for hydrogen sulphide is treated with one tenth of its volume of concentrated hydrochloric acid, a little para-amino-dimethyl-aniline sulphate is added from the point of a knife-blade, stirred into the liquid, and as soon as it has dissolved, one or two drops of a dilute ferric chloride solution is added.

If only 0.0,000,182 gm. of hydrogen sulphide in a liter is present, the blue color is distinctly apparent after half an hour's standing, while the above tests would afford negative results.

If too little hydrochloric acid is present, a red coloration is obtained; this is caused by the action of ferric chloride upon a faintly acid solution of aminodimethylaniline. If considerable hydrochloric acid is present the red coloration does not appear.

8. **Oxidizing Agents**, such as the halogens, nitric acid, chro-

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\* Ber. 16, 2234.



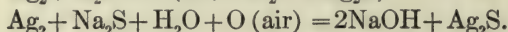
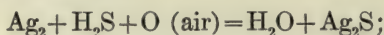
mates, permanganates, ferric salts, etc., decompose hydrogen sulphide with separation of sulphur.

In order to detect the presence of sulphur in insoluble sulphides they may be fused with a little caustic soda (on the cover of a porcelain crucible), when soluble sodium sulphide is formed:



Some sulphate is always formed by this treatment; but the aqueous solution of the melt will always contain enough alkali sulphide for any of the previous tests.

9. **Metallic Silver** is blackened by both free hydrogen sulphide and soluble sulphides:



If oxygen and water are not present, the above reactions will not take place. A piece of bright silver suspended for fourteen hours in a sulphur spring showed no sign of darkening until it had been exposed to the air for a short time.

Absolutely dry hydrogen sulphide, in the presence of absolutely dry oxygen, acts upon silver at ordinary temperatures only very slowly; it acts instantly if a trace of water is present.

### Behavior of the Sulphides on Ignition.

Most sulphides remain unchanged when heated out of contact with the air; arsenic and mercuric sulphides sublime.

The polysulphides lose sulphur, which sublimes. The sulphides of gold and platinum lose sulphur, leaving the metal behind. All sulphides when heated in the air give off sulphur dioxide, which can be recognized by its odor.

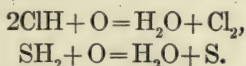
**The Detection of Sulphur in Non-Electrolytes** is usually effected by heating the substance in a glass tube with metallic sodium (cf. page 284), and testing the aqueous extract of the melt with sodium nitroprusside; or, the residue in the tube may be treated with dilute hydrochloric acid and the escaping gas tested with lead acetate paper for hydrogen sulphide.

The following method of testing for sulphur is very certain. The sulphur is converted into sulphuric acid which is precipitated with barium chloride in hydrochloric acid solution. (Cf. page 392). The best way of converting the sulphur into sulphuric acid is to heat with concentrated nitric acid in a sealed tube. (Carius method, see Vol. II) or, in the case of difficultly-volatile substances low in sulphur, by fusion with sodium peroxide in a nickel crucible. Since, however, this last oxidation often takes place with explosive violence, it is best not to use pure sodium peroxide, but to mix it with sodium-potassium carbonate. One part of the substance (from 0.1 to 5 gms. according to the sulphur content) is mixed with 10 parts of sodium-potassium carbonate and 3 parts of sodium peroxide and heated in a nickel crucible. The crucible is inserted in a disk of asbestos board to keep the flame of the gas away from the contents of the crucible; if this precaution is not taken a little sulphate is obtained from the sulphur in the gas. After cooling the melt, it is dissolved in water and the solution filtered; after acidifying with hydrochloric acid, the filtrate is tested for sulphuric acid with barium chloride.

### SULPHUR, S.

*Occurrence.*—Sulphur is found native in volcanic regions in the form of orthorhombic pyramids, and in the neighborhood of sulphur waters, being formed from the oxidation of some of the hydrogen sulphide which escapes.

*Preparation and Properties.*—Like the halogens, sulphur is formed by the oxidation of its hydrogen compound:



By heating polysulphides or the sulphides of the noble metals (gold and platinum), sulphur is also obtained.

Sulphur exists in three allotropic modifications:

1. As *Orthorhombic Sulphur*, with a melting-point of  $114^\circ \text{C}$ ., obtained by crystallization from solutions below  $95^\circ$ .

2. As *Monoclinic Sulphur*, with a melting-point of  $120^{\circ}$  C., obtained by the solidification of molten sulphur.

3. As *Amorphous Sulphur*, obtained by quickly cooling the molten sulphur after it has become viscous by heating to  $250^{\circ}$  C., or after it has become a thin liquid after heating to a higher temperature.

Monoclinic sulphur changes gradually into orthorhombic octahedrons; or, in other words, the unsymmetrical form changes into the symmetrical form. This is a general phenomenon:

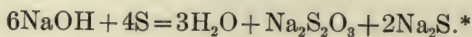
*If a substance exists in two or more crystallographic forms, the more symmetrical form is always the more stable, and the less symmetrical always has a tendency to go over into the more symmetrical form.* Thus the unsymmetrical, orthorhombic, yellow mercuric iodide is changed, by rubbing with a glass rod, into symmetrical, tetragonal, red mercuric iodide (cf. page 170); and, furthermore, the orthorhombic form of calcium carbonate, aragonite, changes into hexagonal calcite.

Both of the *crystalline* modifications of sulphur are soluble in carbon disulphide; and, by evaporating the solution, the sulphur always recrystallizes in the form of octahedrons. Amorphous sulphur is insoluble in carbon disulphide.

Commercial "flowers of sulphur" is a mixture of crystalline and amorphous sulphur, and therefore is only partly soluble in carbon disulphide.

Sulphur burns in the air to sulphur dioxide, and, in the presence of "contact substances," such as platinum, oxide of iron, chromic oxide, etc., it is burned to sulphur trioxide also. Consequently the gas from pyrites burners always contains a mixture of the two gases.

Sulphur is insoluble in water, but soluble in hot caustic alkali, forming a thiosulphate and a sulphide:



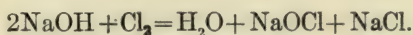
This reaction is entirely analogous to the formation of hypochlo-

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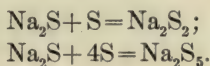
\* By further action of sulphur the  $\text{Na}_2\text{S}$  is changed into  $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_3$ , etc.



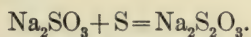
rite and chloride by the action of chlorine upon cold dilute caustic alkali:



Sulphur dissolves on warming with an alkali sulphide, forming polysulphides:



Sulphur is also soluble in alkali sulphites, forming a thiosulphate:



### ACETIC ACID, $\text{CH}_3\text{COOH}$ .

Acetic acid is found in the sap of many plants, partly free and partly in the form of its potassium or calcium salt.

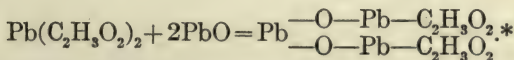
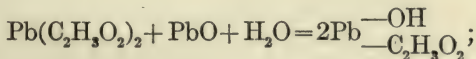
It is formed by the dry distillation of wood or by the oxidation of alcohol.

Anhydrous acetic acid (glacial acetic acid) solidifies below  $+16^\circ\text{C}$ ., forming colorless, glistening plates. It has a penetrating odor, similar to that of sulphur dioxide, and is miscible with water, alcohol, and ether in every proportion. It boils at  $118^\circ\text{C}$ .

The aqueous solution reacts acid. It is a monobasic acid, and its salts, the acetates, are as a rule readily soluble in water; the silver salt is difficultly soluble.

The most important commercial salts of this acid are sodium acetate, and lead acetate (sugar of lead),  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$ .

Neutral lead acetate dissolves lead oxide with the formation of basic salts:




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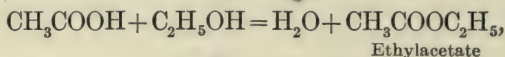
\* The solutions of the soluble basic lead acetates, as well as that of neutral lead acetate, yield precipitates of lead carbonate when acted upon by carbon dioxide. For this reason turbid solutions are often obtained when these salts are dissolved in distilled water, because the latter frequently contains carbonic acid. If a drop of acetic acid is added to the turbid solution the precipitate disappears at once.

## REACTIONS IN THE WET WAY.

A solution of sodium acetate should be used for the following reactions:

1. **Dilute Sulphuric Acid** sets acetic acid free from its salts; it is quite volatile and can be recognized by its odor.

2. **Concentrated Sulphuric Acid** also sets acetic acid free. If alcohol is added at the same time and the mixture warmed, ethyl acetate is formed,



which can be recognized by its pleasant, fruity odor.

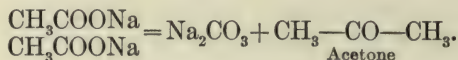
3. **Silver Nitrate** produces, in fairly concentrated solutions, a white crystalline precipitate of silver acetate (100 parts of water dissolve 1.04 parts at 20° C. and 2.52 parts at 80° C.).

4. **Ferric Chloride** colors neutral solutions dark brown, and by boiling the diluted solution, all the iron is precipitated as basic acetate (cf. page 119).

## REACTIONS IN THE DRY WAY.

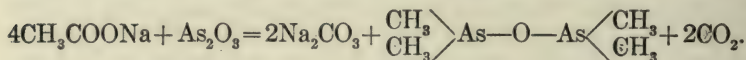
All acetates are decomposed on ignition, leaving behind either the carbonate, oxide, or the metal itself, and with the evolution of combustible vapors and gases.

The acetates of the alkalies are decomposed into carbonate and acetone:



The acetates of the alkaline earths always leave the metal in the form of its oxide, while the acetates of the noble metals leave a residue of the metal itself.

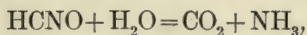
**Cacodyl Reaction.**—If a dry acetate (best an alkali acetate) is heated with arsenic trioxide, a very repulsive-smelling and extremely poisonous gas is formed, called cacodyl oxide:



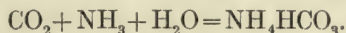
In spite of the sensitiveness of this reaction, it cannot always be relied on, for many other organic acids, such as butyric and valeric acids, give similar reactions.

### CYANIC ACID, HCNO.

This very unstable acid is obtained by heating its polymer, cyanuric acid,  $(\text{HCNO})_3$ ; it is a colorless liquid with a very penetrating, disagreeable odor, which immediately decomposes in aqueous solution into carbonic acid and ammonia,

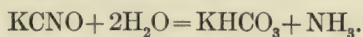


and these two products unite, forming monoammonium carbonate:



The salts of cyanic acid, the cyanates, are much more stable than the free acid, and may be obtained by the oxidation of cyanides.

By simply fusing potassium cyanide in the air, perceptible quantities of potassium cyanate are formed. If, however, potassium cyanide is heated with oxidizing substances, or those which can be readily reduced, it is easy to change the cyanide completely over to cyanate. The cyanates of the alkalis are stable in the dry state, but take on moisture from the air and are gradually changed into monoalkali carbonate and ammonia:



*Solubility of Cyanates.*—The cyanates of the alkalis and alkaline earths are soluble in water. Silver, mercurous, lead, and copper cyanates are insoluble in water. All cyanates are soluble in nitric acid.

### REACTIONS IN THE WET WAY.

A freshly-prepared, cold solution of potassium cyanate should be used for these reactions.

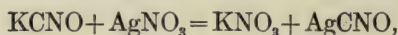
1. **Dilute Sulphuric Acid** immediately sets cyanic acid free, which decomposes (as given above) into carbonic acid and ammonia. Consequently a strong evolution of carbon dioxide takes place on adding the sulphuric acid. The carbon dioxide always contains



small amounts of undecomposed cyanic acid, which is recognizable by its very penetrating odor. The solution will contain ammonium sulphate; so that, if it is warmed with caustic soda, ammonia will be given off.

2. **Concentrated Sulphuric Acid** reacts similarly.

3. **Silver Nitrate** precipitates white, curdy silver cyanate,

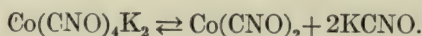


soluble in ammonia and in nitric acid (difference from silver cyanide).

4. **Barium Chloride** produces no precipitation.

5. **Cobalt Acetate** is colored azure blue by a solution of potassium cyanate. The blue potassium cobaltocyanate,  $\text{K}_2[\text{Co}(\text{CNO})_4]$ , discovered by Blomstrand,\* is formed by this reaction, and is obtained in the form of tetragonal crystals of a dark azure blue color.

This blue compound dissolves in water with a blue color. If, however, the blue compound is subjected to the action of considerable water, the color disappears, the double salt being dissociated into its components:



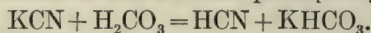
If more potassium cyanate is added to the solution which has become colorless, the blue color reappears. The same result is reached by adding alcohol.

Almost all commercial potassium cyanide contains some cyanate.

In order to detect the presence of cyanate in the commercial salt, the cyanide must first be expelled, for the cobalt test does not take place in the presence of cyanide.

According to E. A. Schneider,† the following process may be used:

Three to five gm. of the potassium cyanide to be tested is dissolved in 30 to 50 c.c. of cold water, and carbon dioxide passed into the solution for one to one and one half hours; the hydrocyanic acid is expelled, and monopotassium carbonate is formed, while the potassium cyanate is not affected perceptibly:

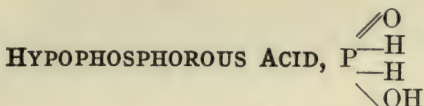


\* Journal für Praktische Chemie [2], 3, 206.

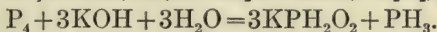
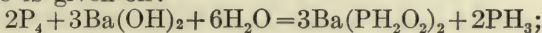
† Ber., 1895, p. 1540.

One c.c. of the solution is now treated with 25 c.c. of absolute alcohol (in order to precipitate potassium carbonate) and the precipitate is filtered off. The alcoholic filtrate is treated with a few drops of acetic acid and then with a few drops of alcoholic cobalt acetate solution.

If the original cyanide contained 0.5 per cent of potassium cyanate, the blue color can be distinctly recognized.\*



The monobasic hypophosphorous acid is obtained by the decomposition of its barium salt with sulphuric acid, or of its calcium salt with oxalic acid. The salts of hypophosphorous acid are obtained by boiling phosphorus with dilute alkali, whereby phosphine is given off:

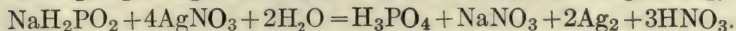
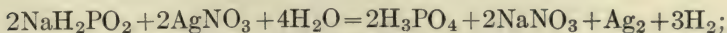


The phosphine thus obtained is spontaneously combustible owing to the presence of small quantities of liquid phosphine,  $\text{P}_2\text{H}_4$ ; it is, however, mixed with considerable hydrogen because the alkali reacts upon the alkali hypophosphite with evolution of hydrogen. See No. 6, below.

*Solubility of Hypophosphites.*—All hypophosphites are soluble in water.

#### REACTIONS IN THE WET WAY.

1. **Dilute Sulphuric Acid.**—No reaction.
2. **Concentrated Sulphuric Acid** reacts with hypophosphites only on warming, and is reduced to sulphur dioxide, which can be recognized by its odor.
3. **Silver Nitrate** is reduced to metallic silver, sometimes with and sometimes without the evolution of hydrogen, according to the relative amounts of the substances reacting:




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\* Experiments made in Zürich by P. Rieder confirm this statement, but the sulphonyanates of the alkalies give the same reaction.

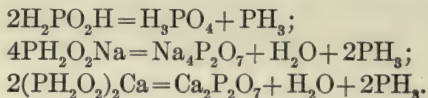
4. **Barium Chloride** causes no precipitation.
5. **Copper,\* Mercury, and Gold Salts** are reduced to metal.
6. **Concentrated Caustic Potash.**—By boiling with concentrated caustic alkali, the hypophosphites are oxidized, with evolution of hydrogen, to phosphates:



7. **Nascent Hydrogen** (zinc and dilute sulphuric acid) reduces hypophosphorous acid to phosphine (see Phosphorous Acid).

#### REACTIONS IN THE DRY WAY.

By ignition phosphate and phosphine are obtained:



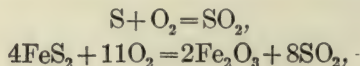
### GROUP III.

**Silver Nitrate** produces a white precipitate, soluble in nitric acid.

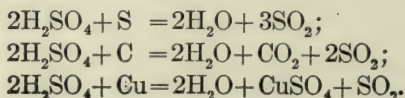
**Barium Chloride** does the same.

#### SULPHUROUS ACID, $\text{H}_2\text{SO}_3$ .

*Occurrence and Preparation.*—Sulphur dioxide, the anhydride of sulphurous acid, is found in the exhalations of active volcanoes, and is formed by the combustion of sulphur or sulphides in the air,



or by the reduction of sulphuric acid on heating with sulphur, sulphides, carbon, organic substances, and metals:



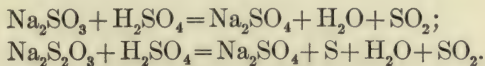

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\* With copper the reduction can go so far that copper hydride is formed. Cf. Würtz, *Compt. rend.* 18, 102.



Mercury, silver, tin, etc., act the same as copper.

Sulphur dioxide is also formed by the decomposition of sulphites and thiosulphates with stronger acids:



Sulphurous acid may be prepared for laboratory purposes by placing a concentrated solution of sodium bisulphite in a flask and allowing concentrated sulphuric acid to drop upon it. A steady stream of sulphur dioxide will be evolved without warming.

Sulphur dioxide is a colorless gas, having the penetrating odor peculiar to burning sulphur, and is readily soluble in water and alcohol: one vol. water at 15° C. dissolves 45.36 vol.  $\text{SO}_2$ ; one vol. alcohol at 15° C. dissolves 116 vol.  $\text{SO}_2$ .

The aqueous solution contains sulphurous acid,  $\text{H}_2\text{SO}_3$ . If we attempt to isolate the acid, it decomposes immediately into water and sulphur dioxide; consequently the free acid is known only in aqueous solution. By neutralization of this solution with alkali hydroxides or carbonates, the comparatively stable sulphites are obtained. *In solution, sulphites are gradually changed into sulphates.*

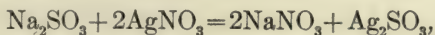
*Solubility of Sulphites.*—The sulphites of the alkalies are readily soluble in water; the remaining sulphites are difficultly soluble or insoluble in water, but are all soluble in hydrochloric acid.

#### REACTIONS IN THE WET WAY.

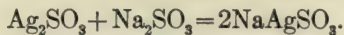
1. **Dilute Sulphuric Acid** evolves sulphur dioxide, in the cold, from all sulphides, the gas being easily recognized by its odor.

2. **Concentrated Sulphuric Acid** reacts in the same way, but much more energetically.

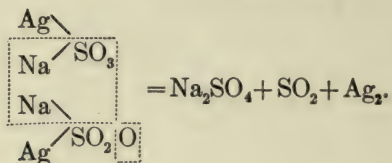
3. **Silver Nitrate** produces, in neutral solutions of sulphites or in an aqueous solution of sulphurous acid, a white crystalline precipitate of silver sulphite,



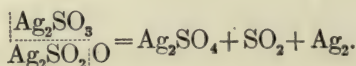
soluble in an excess of the precipitant, forming sodium silver sulphite:



By boiling this solution the silver is precipitated as a gray metal:

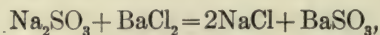


If the water containing silver sulphite in suspension is boiled, half the silver is reduced to metal, while the other half goes into solution as sulphate:

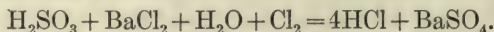


Silver sulphite is soluble also in ammonia and in nitric acid.

4. **Barium Chloride** produces no precipitation in an aqueous solution of sulphurous acid, but in neutral sulphite solutions white barium sulphite is precipitated,



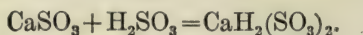
readily soluble in cold, dilute nitric acid. By boiling the solution, barium sulphate is formed slowly and separates out. As the sulphites in aqueous solution are gradually changed to sulphates, commercial sulphites often contain sulphate. In this case the precipitate produced by barium chloride in neutral solution contains barium sulphate, which is insoluble in dilute nitric or hydrochloric acid. If the barium sulphate is filtered off and the filtrate treated with chlorine or bromine water, a white precipitate of barium sulphate is formed, provided a sulphite was originally present:



5. **Strontium and Calcium Salts** behave similarly to the barium salt.

The sulphites of the alkaline earths vary in their solubilities in sulphurous acid and in water.

Calcium sulphite readily dissolves in an excess of sulphurous acid, forming monocalcium sulphite:



On boiling this solution, sulphur dioxide escapes, and calcium sulphite is reprecipitated.

The strontium salt also dissolves in sulphurous acid, but more difficultly; the barium salt is practically insoluble in sulphurous acid.

SOLUBILITY OF THE ALKALINE-EARTH SULPHITES IN WATER.

One part calcium sulphite dissolves in	800 parts water at 18° C.
" " strontium " " "	30,000 " " " 18° C.
" " barium " " "	46,000 " " " 18° C.

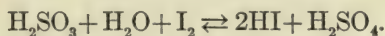
Advantage is taken of the difficult solubility of strontium sulphite in detecting sulphurous acid in the presence of thiosulphuric acid (which see).

6. **Lead Salts** precipitate white lead sulphite, soluble in cold dilute nitric acid; but on boiling the solution lead sulphate is precipitated.

7. **Sodium Nitroprusside and Zinc Sulphate.**—If a neutral sulphite solution is treated with a dilute solution of sodium nitroprusside, a faint pink coloration is produced. If, however, considerable zinc sulphate is added, the coloration becomes a distinct red. The reaction is still more sensitive if a little potassium ferrocyanide is added, a red precipitate being formed (difference from thiosulphuric acid). This reaction, although very delicate, is not so reliable as the precipitation with strontium chloride.

Sulphurous acid is a strong reducing agent.

8. **Iodine Solutions** are decolorized by sulphurous acid:



9. **Acid Potassium Permanganate Solutions** are also decolorized, sulphuric and dithionic acids being formed in varying amounts according to the temperature and concentration.

Under certain conditions the reaction can take place according to the following equations:

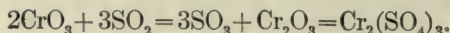


Under other conditions, however, the sulphurous acid can be completely oxidized to sulphuric acid. Consequently, sulphurous

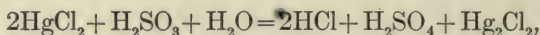


acid cannot be determined quantitatively by means of potassium permanganate.

10. **Chromic Acid** is reduced to green chromic salt:



11. **Mercuric Chloride** is unaffected by sulphurous acid at ordinary temperatures; but, on boiling, it is reduced to mercurous chloride,



and on adding more sulphurous acid, the mercurous salt is reduced to gray metal.

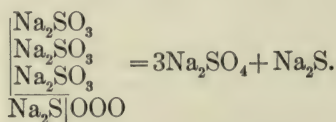
12. **Mercurous Nitrate** is immediately acted upon by free sulphurous acid and by alkali sulphite solutions, with the formation of a black precipitate.

13. **Gold Solutions** are also reduced.

14. **Nascent Hydrogen** reduces sulphurous acid to hydrogen sulphide, which can be recognized by its odor and by its turning lead acetate paper black. The reduction is best effected with zinc and dilute hydrochloric acid.

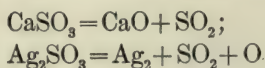
#### REACTIONS IN THE DRY WAY.

The sulphites of the alkalies, when heated out of contact with the air, are changed to sulphate and sulphide:

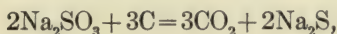


By heating an alkali sulphite in the closed tube this reaction takes place, and there is no sublimate of sulphur (difference from thiosulphates). If the melt is treated with hydrochloric acid after cooling, hydrogen sulphide is given off freely.

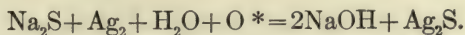
The remaining sulphites are changed, on being heated out of contact with the air, into sulphur dioxide and oxide or metal:



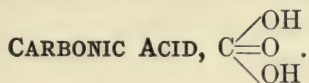
If any sulphite is heated with sodium carbonate on charcoal, sodium sulphide is formed. If the melt is placed upon a bright silver coin and moistened with water, the silver is blackened, owing to the formation of black silver sulphide (Hepar reaction):



and



This Hepar reaction takes place with all sulphur compounds, and therefore shows simply the presence of sulphur.



Like sulphurous acid, pure carbonic acid does not exist; being known only in aqueous solution, which is decomposed, on boiling, into its anhydride, a gas which escapes from the hot solution. This anhydride,  $\text{CO}_2$ , is formed by the combustion of carbon and of carbonaceous matter of all kinds, and is found therefore very widely distributed in nature (in small amounts in the atmosphere, † and in enormous amounts in volcanic regions, streaming out from fissures in the earth). Carbon dioxide occurs also in many mineral waters, and (in the liquid state) is found enclosed in quartz, feldspar, etc. As carbonate it exists in enormous quantities as limestone, marble, aragonite, dolomite, etc. Carbon dioxide is a colorless, odorless, slightly acid-tasting gas, with sp. gr. 1.52. Being, therefore, one and one half times as heavy as air, it can be poured from one vessel into another. It is comparatively soluble in water; one volume of water dissolves at  $0^\circ \text{C}$ . almost twice its volume of carbon dioxide; at ordinary temperatures it dissolves its own volume of gas. Carbon dioxide does not support combustion; a burning candle goes out in air containing 8–10 per cent. of this gas.‡

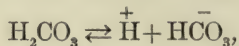
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\* Atmospheric oxygen.

† Pure air contains 0.35–0.40 per cent. of  $\text{CO}_2$ . In dwelling places the amount increases considerably, owing to breathing and other forms of combustion. If 3–4 per cent. is present, as is the case in mines sometimes, breathing becomes difficult, and the miner's lamp begins to burn faintly; while when 8–10 per cent. is present the lamp goes out.

‡ Carbon dioxide not only fails to support combustion, but it tends to prevent it; hence its use in fire-extinguishers. Being formed by the combustion of carbon, the mass-action principle shows that it will tend to stop the reaction much better than an inert gas.

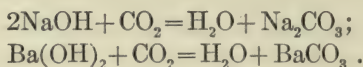
In aqueous solution carbonic acid reacts acid; but its conductivity is extremely small, it being slightly dissociated. It is not decomposed into H and  $\text{CO}_3$  ions, but according to the following equation,



into H and univalent  $\text{HCO}_3$  ions, and this only to a slight extent; by increasing, therefore, the concentration of the H ions (addition of a stronger acid) the carbonic acid is scarcely dissociated at all. If the solution then becomes supersaturated with  $\text{H}_2\text{CO}_3$ , the excess is decomposed into water and carbon dioxide, and the latter escapes from the solution.

The salts of carbonic acid, the carbonates, are formed:

1. By passing carbon dioxide gas into a solution of a metallic hydroxide:

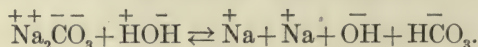


2. By the action of carbon dioxide upon cyanides, sulphides, and borates of the alkalies and alkaline earths.

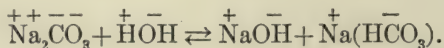
3. By the ignition of salts of organic acids (cf. page 49).

An illustration of the preparation of large amounts of carbonate is the production of potash by burning parts of plants (wood, for example, or the residue from the manufacture of beet sugar, the latter being particularly rich in potassium salts).

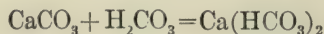
*Solubility of Carbonates.*—Of the normal carbonates, only those of the alkalies are soluble in water; and their aqueous solutions react alkaline, owing to hydrolytic decomposition:



The aqueous solution of the carbonates of the alkalies, therefore, behaves as if it were a solution of caustic alkali and monoalkali carbonate (bicarbonate):

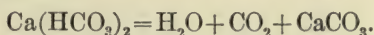


Many carbonates dissolve in an excess of carbonic acid, forming bicarbonates, particularly the alkaline-earth carbonates:





By boiling a solution of calcium bicarbonate, the latter is decomposed into water and carbon dioxide, so that calcium carbonate is reprecipitated:



Nearly all samples of drinking-water contain calcium or magnesium bicarbonate; they become turbid, therefore, on boiling (boiler scale). Dilute, cold mineral acids decompose all carbonates with effervescence (due to evolution of carbon dioxide gas).

The native carbonates of magnesium and iron (magnesite, siderite, and dolomite) do not effervesce if a lump of the mineral is treated with cold dilute mineral acids, but when reduced to a fine powder they are more readily acted upon; on warming, all carbonates dissolve readily.

#### REACTIONS IN THE WET WAY.

1. **Dilute Sulphuric Acid** decomposes all carbonates with effervescence; except with magnesite, siderite, and dolomite, the reaction takes place in the cold. The experiment is best performed by placing a little of the substance in a test-tube, covering it with dilute sulphuric acid, and warming. As carbon dioxide is heavier than air, the gas can be poured into a second test-tube containing a little barium hydroxide or lime water. If now the second test-tube is shaken, a turbidity due to the formation of calcium or barium carbonate will be formed, provided a carbonate was originally present.

A blank test should always be made by pouring some barium hydroxide into a test-tube and shaking it. A turbidity of the latter solution can always be detected, owing to the presence of carbon dioxide in the air. If the turbidity produced in the first case is stronger than that formed in the blank test, carbon dioxide was given off from the substance tested; but if no distinct difference can be detected, the experiment should be repeated in an atmosphere free from carbon dioxide.

To accomplish this, the test-tube containing the original substance is provided with a rubber stopper containing two holes. Through one of the holes the stem of a small separatory funnel is inserted, through which the sulphuric acid can be added; in the

other hole a right-angled glass tube is introduced, so that the end of the tube is level with the lower surface of the rubber stopper. This tube should be loosely filled with cotton wool,\* and connected (by means of rubber tubing) with a second test-tube also provided with a two-holed rubber stopper. Through one of the latter holes a right-angled tube is introduced, extending to the bottom of the tube; in the other hole is placed the stem of a funnel, which contains a folded filter-paper. A stream of air free from carbon dioxide is now conducted through the apparatus for half an hour, the air passing through a solution of caustic potash and then through a tube filled with soda lime before reaching the apparatus. A little barium hydroxide solution is then filtered into the second test-tube, and a little more of the purified air passed through the apparatus in order to make sure that the latter is absolutely free from carbon dioxide (the baryta water should remain clear). Dilute sulphuric acid is now added to the substance, and the purified air is conducted through the apparatus very slowly (two to three bubbles a second). If the solution of barium hydroxide becomes turbid, the presence of a carbonate is assured.

2. **Concentrated Sulphuric Acid** reacts in the same way as dilute sulphuric acid, only more violently.

3. **Silver Nitrate** precipitates white silver carbonate, which becomes yellow on the addition of an excess of the reagent. On boiling with considerable water, the carbonate is partly decomposed into brown silver oxide and carbon dioxide; but the carbonic acid is not completely set free except on heating to 200° C. Silver carbonate is very soluble in ammonia and in nitric acid.

4. **Barium Chloride** precipitates white, voluminous barium carbonate, in the cold, which gradually on standing, but more quickly on warming, becomes crystalline and denser.

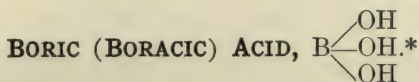
### Behavior of Carbonates on Ignition.

The carbonates of the alkalis melt, with but slight decomposition. Barium carbonate is not decomposed by the blowpipe when placed on charcoal and does not melt; only at a white heat

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\* The wad of cotton wool serves as a filter, preventing any sulphuric acid from being carried over into the second test-tube, which would itself cause a turbidity if it came in contact with the barium hydroxide solution.

is it decomposed into infusible barium oxide and carbon dioxide. All remaining carbonates are decomposed at the temperature of the blowpipe into oxide and carbon dioxide. The oxides of the noble metals are further decomposed into metal and oxygen.



*Occurrence.*—Boric acid is found native as sassolite; in the form of its sodium salt, as borax or tinkal;† as boracite,  $2\text{Mg}_3\text{B}_8\text{O}_{15} + \text{MgCl}_2$ ; and in many silicates, such as axinite, tourmaline, datolite, etc.

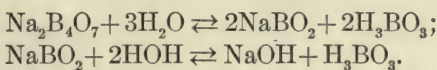
Crystallized boric acid forms colorless plates, with a mother-of-pearl lustre, which are soluble in water (100 parts water dissolve four parts of boric acid at 15° C., and 33 parts at 100° C.). The aqueous solution reacts acid, and is a poor conductor of electricity.

By heating boric acid to 100° C., it loses one molecule of water and is changed to metaboric acid,  $\text{HBO}_2$ . The latter loses more water when heated to 160° C., forming pyroboric acid,  $\text{H}_2\text{B}_4\text{O}_7$ ; which, on ignition, loses all its water, being changed to the anhydride of boric acid, boron trioxide, which remains as a difficultly volatile hygroscopic glass.

The salts of boric acid, the borates, are derived from the meta- and pyroboric acids. The salts of the ortho acid,  $\text{H}_3\text{BO}_3$ , are not known in the pure state.

*Solubility of Borates.*—The borates of the alkalis dissolve in water, and the solution reacts alkaline.

A concentrated solution of borax behaves as if it contained sodium metaborate, free boric acid, and a small amount of caustic alkali:



The more dilute the solution, the greater the extent to which the hydrolysis represented by the second equation will take place; so that a very dilute solution of borax will react as if it contained simply sodium hydroxide and free boric acid.

\* In a few exceptional cases boron acts as a metal, forming  $\text{B}(\text{HSO}_3)_3$ ,  $(\text{BO})_2\text{SO}_4$ ,  $\text{BPO}_4$ , etc. The last compound is insoluble in water and dilute acids, but dissolves readily in caustic alkalis.

†  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .



A solution of an alkali borate will behave differently towards reagents, therefore, according to its concentration and temperature. The remaining borates are difficultly soluble in water, but readily soluble in acids and in ammonium chloride solution.

#### REACTIONS IN THE WET WAY.

For these reactions a solution of borax should be used.

1. **Dilute Sulphuric Acid.**—No reaction.

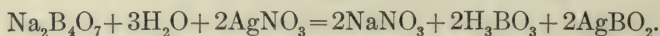
2. **Concentrated Sulphuric Acid.**—No visible reaction. Most borates are decomposed by sulphuric acid, setting free boric acid, and the latter is capable of coloring the non-luminous gas-flame with a characteristic green tinge.

If, therefore, a little solid borate is placed in the loop of a platinum wire, moistened with concentrated sulphuric acid, and heated at the edge of the Bunsen flame, the characteristic green coloration will be noticed.

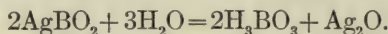
A great many natural silicates containing boric acid, when tested in the above manner, will not give this flame coloration. To produce this coloration the mineral is mixed with calcium fluoride and potassium acid sulphate, placed in the loop of a platinum wire, and heated on the outer edge of the flame, when the latter will be colored distinctly green, owing to the formation of volatile boron fluoride.

3. **Concentrated Sulphuric Acid and Alcohol.**—If an alkali or alkaline-earth borate is treated in a platinum crucible with methyl alcohol, then with concentrated sulphuric acid, the mixture stirred and the alcohol lighted, a green-bordered flame will appear, due to the formation of boric acid methyl ester,  $B(OCH_3)_3$ .

4. **Silver Nitrate** produces, in moderately concentrated cold borax solutions, a white precipitate of silver metaborate:



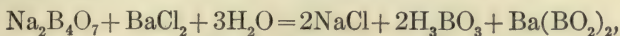
On warming, a brown precipitate of silver oxide is obtained:



From very dilute solutions, in the cold, silver nitrate produces a brown precipitate of silver oxide.

Silver borate is soluble in ammonia and in nitric acid.

5. **Barium Chloride** produces, in fairly concentrated solutions, a white precipitate of barium metaborate:



soluble in an excess of barium chloride and in ammonium chloride.

6. **Calcium and Lead Salts** behave similarly to barium chloride.

7. **Turmeric.**—If a piece of turmeric paper is placed in a solution of free boric acid, apparently no change will take place, but if the paper is dried, it becomes reddish brown.\* If the brown paper is again dipped in the solution of boric acid, the color remains; which is also true if the paper is dipped in a dilute sulphuric or hydrochloric acid solution (difference from the alkali test with turmeric paper). If the reddish-brown paper is moistened with caustic soda or potash solution, the paper becomes bluish black; or, if only a small amount of boric acid is present, grayish blue.† Borate solutions, when acidified with dilute hydrochloric acid, give the same reaction. This sensitive and convenient test for boric acid must be used with caution, for acid solutions of zirconic, titanitic, tantalitic, niobic, and molybdic acids also color turmeric paper brown.

The reaction is much more sensitive if, instead of using the turmeric paper itself, an alcoholic extract is made from a few pieces of turmeric root. Two or three drops of the yellow solution thus obtained are placed in a porcelain dish, the solution to be tested for boric acid is added, acidified with acetic acid, and evaporated to dryness on the water-bath. If as much as  $\frac{2}{1000}$  mg. of  $\text{B}_2\text{O}_3$  is present, the residue is colored a distinct reddish brown, while  $\frac{2}{1000}$  mg. suffices to cause a visible reaction. (F. Henz).

8. **Mercuric Chloride** produces a red precipitate of basic mercuric salt. If considerable free boric acid is present there is no precipitation.

\* Considerable boric acid and sulphuric acid causes the appearance of the brown coloration without the necessity of drying.

† The shade and intensity of the color varies both with the amount of turmeric and with the amount of boric acid; with a very little boric acid, turmeric, and very dilute caustic soda solution a nearly pure violet color is obtained and with considerable boric acid and stronger alkali, a greenish-black color.

### Behavior of Borates on Ignition.

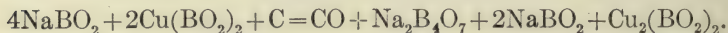
The hydrated borates of the alkalies melt with effervescence, forming a colorless glass.

This glass has the property of dissolving many metallic oxides when heated, whereby the often very characteristically-colored metaborates are formed (borax beads); thus copper oxide is dissolved, forming a blue glass:

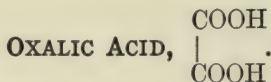
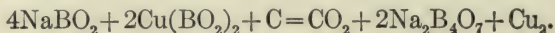


If this bead is heated in the reducing flame (*i.e.*, with carbon) two things can happen:

(a) The colored cupric salt is reduced to colorless cuprous salt:



(b) The cupric salt is reduced to metallic copper, so that the bead appears reddish brown and opaque:



*Occurrence and Preparation.*—Oxalic acid occurs, in the form of its acid potassium and calcium salts, in the sap of many plants.

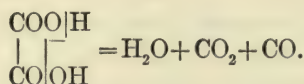
It is prepared in large amounts by fusing sawdust with caustic alkali. The resulting potassium salt is precipitated with milk of lime, forming the insoluble calcium salt; and the latter is decomposed with sulphuric acid. Oxalic acid is also formed by the oxidation of innumerable organic substances (such as sugar, starch, cellulose (paper)), by means of concentrated nitric acid.

It crystallizes from aqueous solutions in the form of colorless monoclinic prisms,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .

By allowing the hydrated acid to stand over sulphuric acid the water is lost, and the anhydrous acid remains, which, when heated to about  $150^\circ \text{C}$ ., sublimes, forming needles. If heated still higher, it



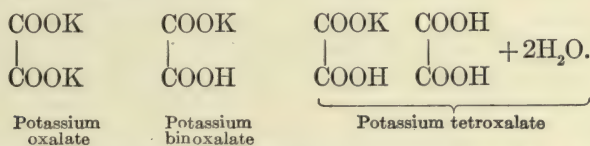
is completely decomposed into water, carbon dioxide, and carbon monoxide:



The crystallized, hydrated acid is soluble in water, alcohol, or ether:

- 100 parts water at 20° C. dissolve 11.1 parts oxalic acid;  
 100 " alcohol at 15° C. dissolve 33.2 parts oxalic acid;  
 100 " ether at 15° C. dissolve 1.5 parts oxalic acid.

Oxalic acid is a fairly-strong, dibasic acid, and forms neutral, acid, and peracid salts:

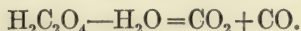


*Solubility.*—The oxalates are mostly insoluble in water, with the exception of the oxalates of the alkalis and of magnesium. In an excess of an alkali oxalate many of the insoluble oxalates dissolve, forming double salts. All oxalates dissolve readily in mineral acids.

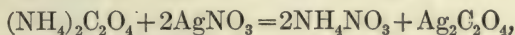
#### REACTIONS IN THE WET WAY.

A solution of ammonium oxalate may be used for the following reactions:

1. **Dilute Sulphuric Acid.**—No reaction.\*
2. **Concentrated Sulphuric Acid,** on warming, acts as a dehydrating agent, causing the evolution of equal volumes of carbon monoxide and carbon dioxide; the latter burns with a blue flame:

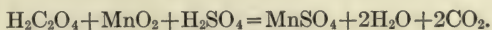


3. **Silver Nitrate** precipitates white, curdy silver oxalate,

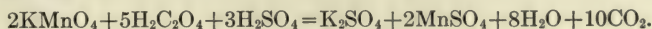



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\* In the presence of manganese dioxide, all oxalates evolve  $\text{CO}_2$  with dilute  $\text{H}_2\text{SO}_4$ :



In the same way  $\text{CO}_2$  is given off by the action of  $\text{KMnO}_4$  and dilute  $\text{H}_2\text{SO}_4$  at about 60° C.:



almost insoluble in water, but readily soluble in ammonia and in nitric acid.

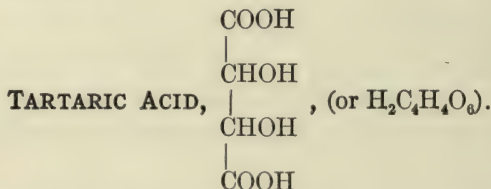
4. **Barium Chloride** precipitates white barium oxalate soluble in oxalic and acetic acids.

5. **Calcium Chloride** precipitates white calcium oxalate, insoluble in oxalic acid, ammonium oxalate, and acetic acid, but readily soluble in hydrochloric and nitric acids. It is the most insoluble of all oxalates.

6. **Lead Salts** precipitate white lead oxalate, soluble in nitric acid.

### Behavior of Oxalates on Ignition.

All oxalates are decomposed on ignition with slight carbonization. The oxalates of the alkalis and barium oxalate are decomposed to carbonate, with the evolution of carbon monoxide. The oxalates of the noble metals, and of iron, nickel, cobalt, copper, etc., leave the metal itself.\*



*Occurrence.*—Tartaric acid occurs partly free and partly as its acid potassium salt in many fruit saps, particularly in that of the grape.

The free acid crystallizes in clear, monoclinic prisms, without water of crystallization. Its aqueous solution is optically active, turning the plane of polarized light to the right.†

Tartaric acid is very readily soluble in water (100 parts water dissolve at 15° C. 132 parts of tartaric acid) and alcohol, but it is insoluble in ether. The salts are called tartrates.

*Solubility.*—The neutral alkali tartrates are very soluble in water,

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\* Strontium oxalate requires the heat of the blast flame to convert it into oxide.

† Three other modifications of this acid exist, possessing the same chemical formula, but differing in their physical properties. One of these turns the plane of polarized light to the left, and the other two are optically inactive.

as also is acid sodium tartrate, while the acid potassium and the acid ammonium tartrates are difficultly soluble in water.

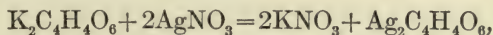
The remaining tartrates are difficultly soluble in water, but all dissolve, more or less readily, in neutral alkali tartrate solution, forming complex salts.

The most important commercial salts of this acid are "cream of tartar," "Rochelle salt," and "tartar emetic."

#### REACTIONS IN THE WET WAY.

A solution of Rochelle salt (sodium potassium tartrate) may be used for these reactions.

1. **Dilute Sulphuric Acid.**—No reaction.
2. **Concentrated Sulphuric Acid** causes carbonization on warming, with evolution of sulphur dioxide.
3. **Silver Nitrate** produces no precipitation in a solution of free tartaric acid, but in the solution of a neutral tartrate, a white, curdy precipitate is immediately formed,



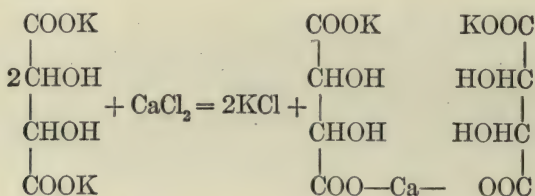
readily soluble in nitric acid and in ammonia. By warming the ammoniacal silver solution, metallic silver is deposited. This very important reaction for the detection of tartaric acid is performed in the following manner:

The pure tartrate solution is treated with nitrate of silver until no further precipitation takes place, when dilute ammonia is added drop by drop until the precipitate just dissolves; and the test-tube containing the solution is then placed in water which has a temperature of 60–70° C. After standing for fifteen minutes (twenty at the latest), the silver will be deposited in the form of a beautiful mirror on the sides of the test-tube. This very delicate reaction cannot be performed with certainty in the presence of other acids. In this case the tartaric acid should first be precipitated as acid potassium tartrate, by treating the solution (which has been concentrated as much as possible) with solid potassium carbonate until alkaline, whereby the tartaric acid is changed to soluble potassium tartrate. If the solution is carefully acidified with concentrated acetic acid, a precipitate of acid potassium tar-

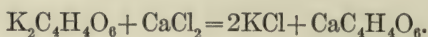


trate will form at once if considerable tartrate is present;\* this is filtered off, washed with a little cold water, and dissolved in as little caustic soda solution as possible. In this way a solution is obtained which will readily give the silver mirror on the addition of silver nitrate and treatment as above.

**4. Calcium and Barium Chloride.**—If to a concentrated solution of neutral alkali tartrate, in the absence of ammonium salts, calcium chloride is added drop by drop, a white amorphous precipitate is formed which redissolves, forming readily soluble calcium alkali tartrate:



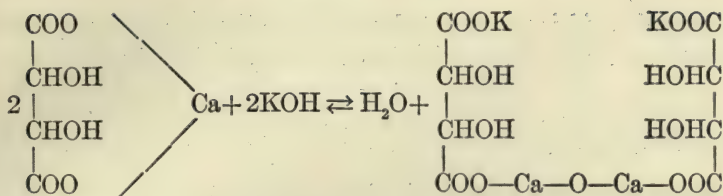
Only after the addition of enough calcium chloride to completely decompose the alkali tartrate is a permanent precipitate formed, which at first is flocculent, but soon becomes crystalline, consisting of neutral calcium tartrate:



In dilute solutions the first addition of calcium chloride often produces no precipitation; but after standing some time (or more quickly on rubbing the sides of the test-tube with a glass rod) the crystalline precipitate is deposited,  $\text{CaC}_4\text{H}_4\text{O}_6 + 4\text{H}_2\text{O}$ . Calcium tartrate is very difficultly soluble in water; 100 parts water at 15° C. dissolve 0.0159 part of the crystalline salt, and 100 parts boiling water dissolve 0.0285 part of the salt. The precipitate is soluble in acetic acid (difference from calcium oxalate) and also in a solution of concentrated caustic alkali (free from carbonate), probably forming a complex salt:

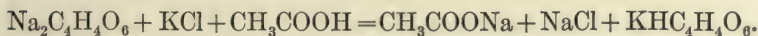
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\* If no precipitate is formed on the addition of the acetic acid, a little alcohol is added, which causes the precipitate to form at once. It is filtered off, washed with diluted alcohol, dried, dissolved in dilute sodium hydroxide, and treated as above. If the alcohol is not removed by drying, a mirror is sometimes formed when tartaric acid is absent.



On boiling this solution, calcium tartrate is reprecipitated in the form of a voluminous gelatinous precipitate, which again goes into solution on cooling. The presence of ammonium chloride retards the formation of the calcium tartrate, but does not prevent it; after standing some time, the precipitate settles out in the form of a heavy crystalline powder (difference from citric acid).

5. **Potassium Salts** produce no precipitation in neutral solutions of alkali tartrates; but if the solution is acidified with acetic acid, a precipitate of crystalline acid potassium tartrate\* is formed immediately or after standing some time, according to the concentration of the solution:



The acid potassium tartrate is difficultly soluble in water (100 parts water dissolve 0.45 part of salt) and in acetic acid, but is readily soluble in mineral acids or in caustic alkali and alkali carbonate solutions.

If a concentrated solution of free tartaric acid is treated with potassium chloride, a precipitate of acid potassium tartrate is formed in spite of the presence of the hydrochloric acid which is set free. From dilute solutions the precipitate appears only after adding sodium acetate (cf. page 48).

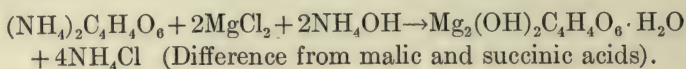
6. **Lead Acetate** produces in neutral solutions a white, flocculent precipitate of lead tartrate, easily soluble in nitric acid and in ammonia.

7. **Magnesia Mixture.** If a concentrated tartaric acid solution is treated with an excess of magnesia mixture, 10 c.c. of strong ammonia and a volume of alcohol equal to that of the solution, then, after shaking and allowing to stand 12 hours,

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\* Cream of tartar.

the tartaric acid is precipitated quantitatively as crystalline, basic magnesium tartrate, insoluble in 50 per cent. alcohol:\*



A silver mirror can be obtained from this precipitate after washing it well with 50 per cent alcohol and drying it, by placing it in a test-tube, rubbing it up with silver nitrate solution, with a glass stirring rod, and heating to 60° on the water-bath.

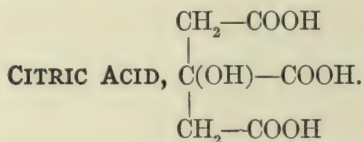
#### REACTIONS IN THE DRY WAY.

If tartaric acid is heated to 135° C., it fuses, and on stronger ignition it is decomposed, leaving a residue of carbon and giving off empyreumatic odors (smell of burnt sugar).

The alkali tartrates are also decomposed by ignition, leaving a residue of carbon and alkali carbonate, which effervesces on treatment with acid.

Ammonium tartrate leaves a residue of carbon, which does not effervesce on treatment with acids. The tartrates of the alkaline earths leave behind a mixture of carbon and carbonate; on very strong ignition the latter is changed to oxide.

The tartrates of those metals whose oxides are reduced by carbon are left in the form of metal (Ag, Pb, Fe, Ni, Co, etc.).



Citric acid is found in nature in the juices of many fruits. It is a tribasic acid, readily soluble in water and in alcohol, but difficultly soluble in ether. Its salts are called citrates.

*Solubility.*—The citrates of the alkalis are readily soluble in water, and form, with the insoluble citrates of the heavy metals, readily soluble complex salts, whose solutions are not precipitated by alkali hydroxides, alkali carbonates, ammonia, etc.

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\* L. v. Ferentzy, Chem. Ztg., 1907, 1118.]



## REACTIONS IN THE WET WAY.

A solution of potassium citrate may be used.

1. **Dilute Sulphuric Acid.**—No reaction.

2. **With Concentrated Sulphuric Acid** carbonization and evolution of sulphur dioxide take place on warming.

3. **Silver Nitrate** produces in neutral solutions a flocculent precipitate of silver citrate,  $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7$ , readily soluble in nitric acid and in ammonia. On heating the ammoniacal solution to  $60^\circ \text{C}$ ., no silver mirror is formed; but on heating the solution to boiling, the silver is gradually deposited.

4. **Barium and Calcium Chloride** give no precipitation in neutral solutions (difference from tartaric acid). If, however, caustic soda solution is added to the solution which contains an excess of calcium chloride, a flocculent precipitate of tertiary calcium citrate is at once formed, insoluble in caustic alkali, but readily soluble in ammonium chloride. On boiling the solution in ammonium chloride, crystalline calcium citrate is precipitated, which is now insoluble in ammonium chloride.

5. **Lime Water** in excess produces no precipitation in solutions of neutral citrates; but on boiling a flocculent precipitate of calcium citrate is formed, which almost entirely redissolves on cooling.

6. **Lead Acetate** precipitates from solutions of the free acid, and those containing neutral salts, amorphous  $\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot \text{H}_2\text{O}$ .

7. **L. Stahre's Test for Citric Acid.\*** A solution containing free citric acid in water, or of a citrate in very dilute sulphuric or nitric acid (not hydrochloric acid), is treated with from 2 to 5 drops of tenth-normal permanganate solution and heated a short time at  $30^\circ$  to  $40^\circ$  (the solution must not boil!). As soon as the solution is colored brown, or becomes turbid by the precipitation of a little manganese dioxide, 1 or 2 drops of ammonium oxalate solution are added and about one c.c. of 10 per cent sulphuric acid, which will clear up the solution. Now, upon the addition of a few drops of bromine water, a distinct, crystalline precipitate of pentabremacetone will be obtained.

This test is not quite so sensitive as the following one, but Wöhler succeeded in detecting 0.3 mgm. of citric acid in 1 c.c. of water.

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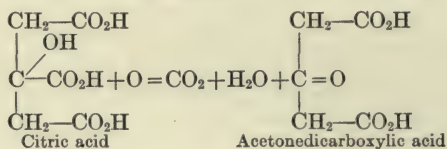
\* L. Stahre, *Z. anal. Chem.*, **36**, 195 (1897); also Alfred Wöhler, *ibid.*, **41**, 94 (1902).

The experiment succeeds in the presence of tartaric, malic, oxalic, sulphuric and phosphoric acids, except that a little more permanganate is required.\*

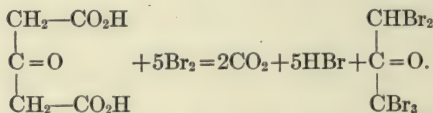
8. **Mercuric Sulphate.**—Denigès' reagent†: 5 gm. HgO dissolved in 100 c.c. of water and 20 c.c. conc. H<sub>2</sub>SO<sub>4</sub>. The solution of the citrate is treated with 1/20 as much reagent and heated to boiling, after which a few drops of N/10 KMnO<sub>4</sub> solution are added. A white crystalline precipitate is formed. The test is sensitive and can be made in the presence of tartaric, malic, oxalic,

\* In the Stahre test the following reactions take place:

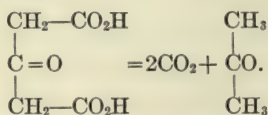
(a) The permanganate oxidizes the citric acid to acetonedicarboxylic acid with evolution of carbon dioxide:



(b) The acetonedicarboxylic acid reacts with bromine, forming pentabromacetone:

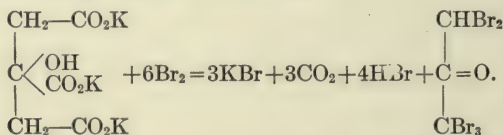


If the permanganate is allowed to act longer upon the citric acid the acetonedicarboxylic acid is converted gradually into acetone, the reaction taking place more quickly on boiling.



Acetone itself is not brominated as readily as the acetonedicarboxylic acid, and for this reason care should be taken not to let the temperature rise above 40° during the treatment of the citric acid with permanganate.

The citrates on treatment with bromine, without previous oxidation with permanganate, will give pentabromacetone:

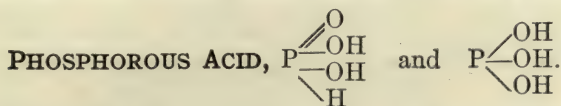


† Comptes rend., 138, 32; Z. anal. Chem., 38, 718 (1899); and 40, 121 (1901).

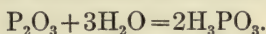
sulphuric, and phosphoric acids\* except that somewhat more permanganate must be added.

#### REACTIONS IN THE DRY WAY.

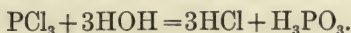
The citrates, on ignition, behave exactly like the tartrates.



*Formation.*—By the slow combustion of phosphorus in the air phosphorus trioxide is formed, being the anhydride of phosphorous acid, which it forms on treatment with cold water:



Phosphorous acid is formed much more readily by the action of water on the trihalogen compounds of phosphorus:



The hydrochloric acid is removed by evaporation, and the last traces of uncombined water by heating to  $180^\circ \text{C}$ . If the mass is then allowed to cool, it solidifies to a crystalline, hygroscopic substance which melts at  $70^\circ \text{C}$ .

By neutralizing the solution of phosphorous acid with bases, the phosphites are obtained. It is never possible, however, to replace more than two of the hydrogen atoms with metal; so that phosphorous acid † is considered a dibasic acid.

*Solubility.*—Only the phosphites of the alkalis are soluble in water, but they are all soluble in acid.

#### REACTIONS IN THE WET WAY.

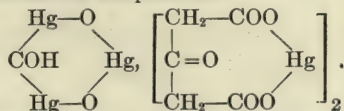
A solution of sodium phosphite should be used.

1. **Dilute Sulphuric Acid.**—No reaction.

2. **Concentrated Sulphuric Acid** causes no reaction in the cold; on heating, the phosphorous acid reduces the sulphuric acid to sulphurous acid, easily recognized by the odor of burning sulphur,  $\text{H}_3\text{PO}_3 + \text{H}_2\text{SO}_4 = \text{H}_3\text{PO}_4 + \text{H}_2\text{O} + \text{SO}_2$ .

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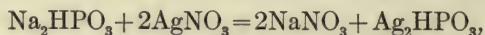
\* This precipitate has the composition:



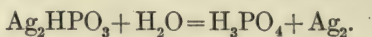
† Certain organic compounds are known, however, which are derived from tribasic phosphorous acid,  $\text{P}(\text{OH})_3$ .



3. **Silver Nitrate** produces at first a white precipitate of silver phosphite,



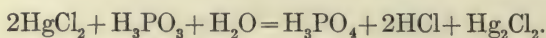
which in the case of a concentrated solution is changed in the cold to metallic silver; while in dilute solutions this reduction takes place only on warming:



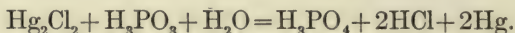
4. **Barium Chloride** precipitates white barium phosphite, soluble in all acids.

5. **Lead Acetate** precipitates white lead phosphite, insoluble in acetic acid.

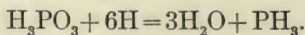
6. **Mercuric Chloride** is slowly reduced by phosphorous acid in the cold, but more quickly on warming, to mercurous chloride:



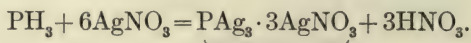
If the phosphorous acid is present in excess, the reduction in the hot solution (not in the cold) goes further, and gray metallic mercury is deposited:



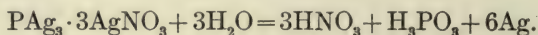
7. **Nascent Hydrogen** (zinc and sulphuric acid) reduces phosphorous acid to phosphine:



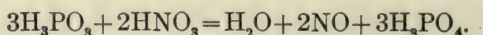
If the phosphine is allowed to act upon a concentrated solution of silver nitrate (1 : 1), or better still, upon solid silver nitrate, the latter is colored yellow, as with arsine:



By the addition of water this yellow compound is decomposed with separation of grayish-white silver:

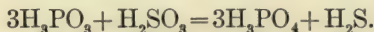


The phosphorous acid is, however, immediately oxidized by the nitric acid to phosphoric acid:



The mixture of phosphine and hydrogen burns with an emerald-green flame.

8. **Sulphurous Acid** is reduced by phosphorous acid to hydrogen sulphide:



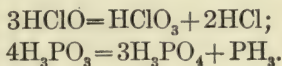
9. **Concentrated Potassium Hydroxide Solution** changes a phosphite over to phosphate, with evolution of hydrogen,



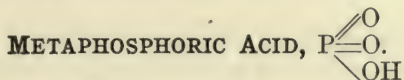
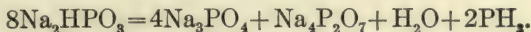
but with dilute caustic potash the hydrogen evolution is very slight.

#### REACTIONS IN THE DRY WAY.

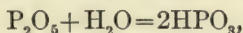
By ignition, phosphorous acid (like hypochlorous acid) is changed at the cost of its own oxygen to the higher compound, while the oxidizing part of the acid is reduced to its hydrogen compound:



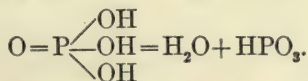
The phosphites behave similarly:



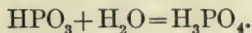
The monobasic metaphosphoric acid is obtained by treating phosphorus pentoxide with cold water,



and also by the strong ignition of orthophosphoric acid:



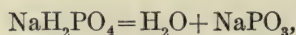
Metaphosphoric acid is a colorless, glassy, hygroscopic mass. On boiling its aqueous solution,\* it adds water to the molecule, and is changed to orthophosphoric acid:



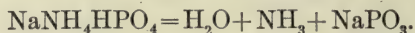

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\* Or slowly in the cold.

The metaphosphates are readily obtained by heating the mono-metallic salts of orthophosphoric acid,



or by igniting sodium ammonium phosphate:



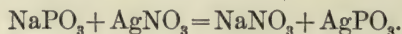
The meta salts are changed into orthophosphates by boiling the aqueous solution in the presence of mineral acid.

*Solubility.*—The metaphosphates of the alkalis and of magnesium are soluble in water; the remaining salts are difficultly soluble or insoluble in water, readily soluble in nitric acid, and in an excess of metaphosphoric acid or an excess of alkali metaphosphate.

#### REACTIONS IN THE WET WAY.

Sodium metaphosphate is used for the following tests.

1. **Sulphuric Acid** causes no visible reaction.
2. **Silver Nitrate** precipitates white silver metaphosphate, soluble in ammonia and in nitric acid:



3. **Barium Chloride** precipitates voluminous barium metaphosphate, which is soluble in an excess of sodium metaphosphate, from which solution ammonia causes no precipitation. Barium sodium dimetaphosphate (or a similar polymetaphosphate) is probably formed.

4. **Magnesium Salts** cause no precipitate from moderately dilute solutions, even on boiling (difference from orthophosphoric acid).

5. **Ammonium Molybdate** produces no precipitate in the cold; but on boiling the acid solution metaphosphoric acid is changed to orthophosphoric acid, and the characteristic precipitate of ammonium phosphomolybdate is formed.

6. **Albumin Solution** is coagulated by an aqueous solution of the free acid (difference from pyro- and orthophosphoric acids), but not by a solution of alkali metaphosphate, except on the addition of acetic acid.

7. **Nascent Hydrogen** does not reduce metaphosphoric acid (difference from phosphorous acid).



**Behavior on Ignition.**

The alkali metaphosphates form, on fusion, a glassy mass, which has the property of dissolving many metallic oxides, with the formation of orthophosphates of characteristic colors. (See Phosphoric Acid.) By fusion with soda, orthophosphates are formed from metaphosphates.

**PYROPHOSPHORIC ACID,  $H_4P_2O_7$ .**

The tetrabasic pyrophosphoric acid is formed by heating orthophosphoric acid to  $213^{\circ}C$ . It is a soft, glassy mass, readily soluble in water; and in solution it gradually adds water to the molecule and is changed to phosphoric acid, the change taking place quickly on boiling the solution.

The salts of pyrophosphoric acid, the pyrophosphates, are obtained by igniting the dimetallic phosphates:



*Solubility.*—The pyrophosphates of the alkalies are soluble in water; the remaining pyrophosphates are difficultly soluble or insoluble in water, but are all soluble in acids, and some are soluble in an excess of sodium pyrophosphate.

**REACTIONS IN THE WET WAY.**

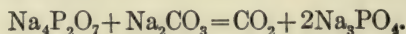
A solution of sodium pyrophosphate is used for these tests.

1. **Sulphuric Acid.**—No reaction.
2. **Silver Nitrate** gives a white, curdy precipitate, soluble in ammonia and in nitric acid.
3. **Barium Chloride** causes a white, amorphous precipitate, soluble in acids.
4. **Magnesium Chloride** produces a white precipitate which is soluble in an excess of the magnesium salt, as well as in an excess of sodium pyrophosphate. By boiling this solution a precipitate is formed, which does not disappear on cooling.
5. **Ammonium Molybdate** produces no precipitation in the cold; but, on warming, yellow ammonium phosphomolybdate is precipitated.

6. **Albumin** is not coagulated by free pyrophosphoric acid (difference from metaphosphoric acid).

#### BEHAVIOR IN THE DRY WAY.

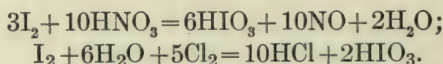
All pyrophosphates on being fused with sodium carbonate are changed to orthophosphates:



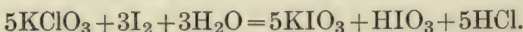
#### IODIC ACID.

*Occurrence.*—In sea-water and in Chili saltpetre as potassium iodate.

*Formation.*—By oxidizing iodine with fuming nitric acid or by the action of chlorine upon iodine suspended in water:



The most important iodate,  $\text{KIO}_3$ , is obtained by the action of iodine upon a slightly acid solution of potassium chlorate:



Iodates are also formed by the action of iodine upon alkali hydroxide solutions:



In alkaline solutions iodides are oxidized to iodates by hypochlorites and potassium permanganate.

*Solubility.*—The iodates of the alkalies are soluble in water, but the remaining iodates are difficultly soluble or insoluble.

#### REACTIONS IN THE WET WAY.

1. **Sulphuric Acid.**—Neither dilute nor concentrated sulphuric acid decomposes iodic acid; but if reducing substances are present at the same time (such as hydriodic acid, hydrogen sulphide, ferrous salts, etc.), the hydriodic acid is reduced, with separation of iodine:



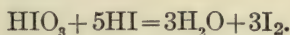
2. **Silver Nitrate** precipitates white, curdy silver iodate,  $\text{AgIO}_3$ , readily soluble in ammonia. but difficultly soluble in nitric acid.

3. **Barium Chloride** precipitates white barium iodate, difficultly soluble in hot water (100 parts of boiling water dissolve 0.6 part of the salt), and only slowly soluble in hydrochloric or nitric acids.

4. **Lead Acetate** precipitates lead iodate, difficultly soluble in water and only slightly soluble in nitric acid.

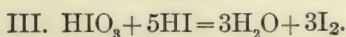
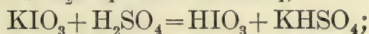
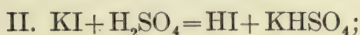
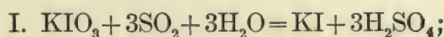
5. **Reducing Agents.**

(a) *Hydriodic acid* reduces iodic acid, with separation of iodine:

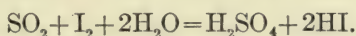


If the solution is concentrated, the iodine separates out as a brown powder; dilute solutions are colored yellow. The iodine may be absorbed with a reddish-violet color by shaking the solution with chloroform or carbon disulphide.

(b) *Sulphurous acid* also causes separation of iodine, unless a large excess of sulphurous acid is added. The reaction takes place in three stages:



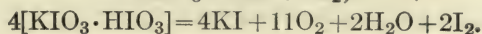
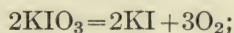
If too much sulphurous acid is added, there will be no permanent deposition of iodine, for it will be changed to hydriodic acid:



(c) *Zinc dust* (or, better, Devarda's alloy) reduces neutral iodate solutions to iodide.

REACTIONS IN THE DRY WAY.

Heated on charcoal the iodates deflagrate, but not so strongly as the chlorates; they are all decomposed on being heated, some with and some without the separation of iodine. Thus all neutral iodates of the alkalis are easily decomposed into iodide and oxygen, while the biiodates set free iodine at the same time:

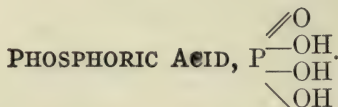




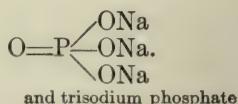
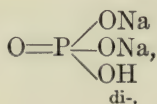
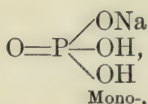
## GROUP IV.

**Silver Nitrate** produces a colored precipitate in neutral solutions, soluble in nitric acid.

**Barium Chloride** also produces a precipitate which is soluble in nitric acid.



Orthophosphoric acid is obtained by the oxidation of phosphorus by means of nitric acid, or by boiling the meta- and pyrophosphoric acids with water. It is a tribasic acid, and forms salts in which either one, two, or three of its hydrogen atoms are replaced by metals:



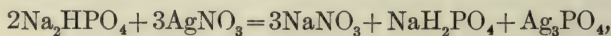
**Solubility.**—The phosphates of the alkalis are soluble in water, and so are the primary salts of the alkaline earths. Their secondary phosphates are very difficultly soluble, while their tertiary phosphates (as well as all other phosphates) are insoluble. All phosphates dissolve in acids.

## REACTIONS IN THE WET WAY.

A solution of disodium phosphate should be used for these reactions.

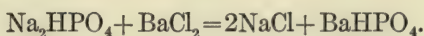
1. **Sulphuric Acid**, dilute or concentrated, produces no visible change.

2. **Silver Nitrate** produces a yellow precipitate of silver phosphate (difference from meta- and pyrophosphoric acids),

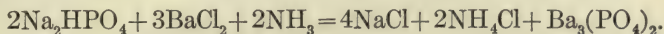


readily soluble in nitric acid and in ammonia. The precipitate, therefore, can only be formed in neutral solution.

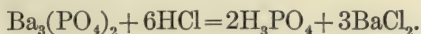
3. **Barium Chloride** precipitates white, amorphous barium phosphate:



In the presence of ammonia the tertiary salt is precipitated:

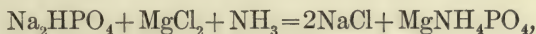


The barium phosphates (as well as those of the other alkaline earths) are easily dissolved by acids, even acetic acid (difference from aluminium and ferric phosphates). From these acid solutions, ammonia reprecipitates the phosphate:



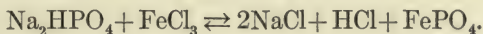
By adding ammonia the phosphoric acid is changed to ammonium phosphate, which precipitates the barium chloride, forming insoluble barium phosphate.

4. **Magnesia Mixture** (a mixture of ammonium chloride, ammonia, and magnesium chloride) precipitates from very dilute solutions white, crystalline magnesium ammonium phosphate,  $\text{MgNH}_4\text{PO}_4 + 6\text{H}_2\text{O}$ ,

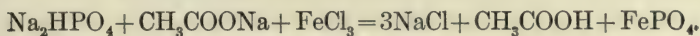


which is soluble in all acids, but practically insoluble in dilute  $2\frac{1}{2}$  per cent. ammonia. This is a very sensitive reaction (cf. page 44).

5. **Ferric Chloride**.—If a solution of sodium phosphate is treated with ferric chloride, a yellowish-white precipitate of ferric phosphate is formed:



As hydrochloric acid is set free by this reaction, the precipitation of the phosphoric acid cannot be quantitative, ferric phosphate being soluble in hydrochloric acid. If some sodium acetate is added to the solution, the amount of free hydrochloric acid is diminished; in its place an equivalent amount of acetic acid is formed, which does not dissolve ferric phosphate; in that case all the phosphoric acid will be precipitated:

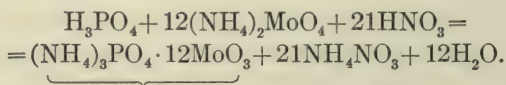


Ferric phosphate is not inappreciably soluble in ferric chloride and ferric acetate solutions; consequently the precipitate is produced in a boiling solution, and as slight an excess as possible of ferric chloride is added. In this way the excess of the ferric chloride will be precipitated as basic ferric acetate with the ferric phosphate, so that it can exert no solvent action. If the solution is filtered hot, a filtrate free from iron and phosphoric acid is obtained.

As ferric phosphate is insoluble in acetic acid, it is evident that phosphoric acid can be completely precipitated from solutions of those phosphates which are soluble in acetic acid by adding ferric chloride, and, thus, separated from the metals with which it was originally combined (*e.g.*, calcium, strontium, barium, and magnesium phosphates).

To accomplish this, the phosphate is dissolved in as little hydrochloric acid as possible, ammonium carbonate is added until a slight permanent precipitate is obtained, which is dissolved by the addition of one or two more drops of hydrochloric acid; ammonium acetate is then added, and ferric chloride drop by drop until the solution above the yellowish-white precipitate of ferric phosphate is colored distinctly brown. The solution is diluted considerably with water, heated to boiling, and filtered hot. In order to detect phosphoric acid in the precipitate, it is dissolved in dilute nitric acid, evaporated to a small volume, and treated with ammonium molybdate, whereby yellow, crystalline ammonium phosphomolybdate is formed (see below); or the precipitate is dissolved in dilute hydrochloric acid, two gms. of tartaric acid are added, and ammonia to alkaline reaction (the iron will not be precipitated, *cf.* page 119). From the ammoniacal solution the phosphoric acid may be precipitated with magnesia mixture as magnesium ammonium phosphate.

6. **Ammonium Molybdate**, in large excess, precipitates from nitric acid solutions in the cold on standing (more quickly on slightly warming) a yellow, crystalline precipitate of ammonium phosphomolybdate:

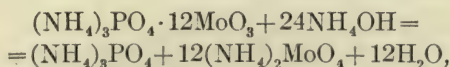


This reaction is completely analogous to the reaction with arsenic acid (*cf.* page 217), with the difference that the arsenic compound



is only formed quickly at the boiling temperature. The presence of ammonium nitrate greatly facilitates the formation of this precipitate.

Ammonium phosphomolybdate is readily soluble in alkalies and in ammonia,



also in an excess of alkali phosphate solutions, forming compounds which contain less molybdenum. It is, therefore, always necessary to prevent the formation of such compounds by the addition of a large excess of ammonium molybdate.

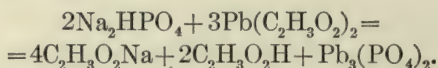
*Detection of Phosphorus in Iron and Steel.*—Phosphorus is present in iron and steel as iron phosphide, but only to a slight extent (usually less than 0.1 per cent.). The detection of the phosphorus is effected by its oxidation to phosphoric acid and using one of the above reactions. As, however, very small amounts of phosphorus are present, it is necessary to start with a large amount of the original substance in order to obtain a perceptible phosphorus test. It is best to proceed as follows: Five to ten grams of the iron or steel are dissolved in about 60 c.c. of nitric acid (sp. gr. 1.2),\* the solution evaporated to dryness and then ignited over a free flame (with constant stirring) until no more red fumes are given off. All organic matter is thereby destroyed, and the silicic acid is dehydrated. After cooling, the oxides are dissolved in 50–60 c.c. of concentrated hydrochloric acid (warming gently), the excess of the acid is removed by evaporation, water is added, and the silica filtered off. In the filtrate all the iron and all the phosphoric acid will be found, and the latter may be detected by either the molybdate or the magnesia-mixture reaction. In order to detect the phosphoric acid according to the former method, the filtrate obtained after the removal of the silica is evaporated to dryness, dissolved in as little nitric acid as possible (sp. gr. 1.2), 50 c.c. of ammonium molybdate solution and 15–20 c.c. of a 75 per cent. ammonium nitrate solution added, the mixture warmed gently and allowed to stand twelve hours. A yellow, crystalline precipitate shows the presence of phosphorus.

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\* If the iron were dissolved in HCl or H<sub>2</sub>SO<sub>4</sub>, part or even all of the phosphorus would escape as phosphine. Nitric acid oxidizes all of the phosphorus to phosphoric acid.

In order to detect the phosphorus according to the magnesia-mixture method, it is necessary first to remove the greater part of the iron. For this purpose the hydrochloric acid filtrate is neutralized with ammonia, a saturated solution of sulphur dioxide is added, and the mixture boiled, whereby the previously dark-colored solution is either decolorized or becomes a light green. Twenty c.c. of concentrated hydrochloric acid are added, and the solution is boiled until the excess of sulphur dioxide is expelled. By this operation all the ferric salt has been reduced to ferrous salt. A few drops of chlorine water are now added (which forms a little ferric salt), the solution is neutralized with ammonia and diluted to about a liter; three c.c. of a saturated solution of ammonium acetate are added, also five c.c. of acetic acid, and the solution heated to boiling, whereby all the ferric salt and all the phosphoric acid will be precipitated in the form of ferric phosphate and basic ferric acetate, while the greater part of the iron remains in solution as ferrous salt. The slightly-brown precipitate is filtered off through a small plaited filter, washed with hot water, dissolved in dilute hydrochloric acid, evaporated almost to dryness, two gm. of citric (or tartaric) acid added (which should be dissolved in as little water as possible), the solution saturated with ammonia, and the phosphoric acid precipitated by the addition of magnesia mixture. A white crystalline precipitate shows the presence of phosphoric acid.

7. **Lead Acetate** precipitates white lead phosphate, nearly insoluble in acetic acid:



8. **Nascent Hydrogen** does not reduce phosphoric acid (difference from phosphorous and hypophosphorous acids).

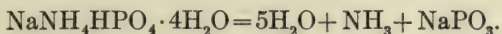
9. **Metastannic Acid**.—If metallic tin is added to a nitric acid solution of phosphoric acid, or a phosphate, the tin is changed to metastannic acid, which unites with the phosphoric acid, forming an insoluble compound (probably a complex phospho-stannic acid). This reaction is often used to separate phosphoric acid from other metals.

10. **Mercurous Nitrate** precipitates from solutions which are almost neutral, white mercurous phosphate, soluble in nitric acid but insoluble in acetic acid.

## REACTIONS IN THE DRY WAY.

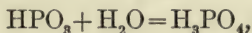
The tertiary salts of the alkalis melt without decomposition; the secondary salts lose water and are changed to pyrophosphates; while the primary salts form a glassy metaphosphate.

The so-called "salt of phosphorus," or "microcosmic salt,"  $\text{NaNH}_4\text{HPO}_4 + 4\text{H}_2\text{O}$ , which is much used as a reagent, loses water and ammonia on being fused, forming a clear glass of sodium metaphosphate:

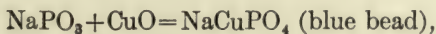


If the salt is heated in the loop of a platinum wire, a clear bead is obtained—the so-called "salt of phosphorus" bead.

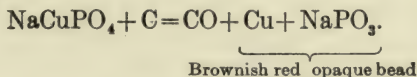
Just as metaphosphoric acid unites with water, on boiling its solution, forming orthophosphoric acid,



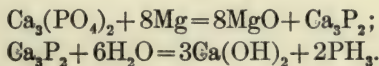
so sodium metaphosphate dissolves, on fusing, a great many metallic oxides, forming characteristically-colored orthophosphates,



which may be changed in the reducing flame to metaphosphate again:



Many anhydrous phosphates are reduced by heating with magnesium to phosphides, which, on being breathed upon, give the peculiar odor of phosphine:



**PHOSPHORUS, P.** At. Wt. 31.04. Mol. Wt.  $\text{P}_4 = 124.16$ .

*Occurrence.*—Phosphorus is found in nature only in the form of phosphates, of which calcium phosphate is the most important. It occurs as apatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{ClF})$ , in hexagonal crystals, and in an



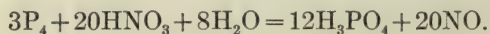
impure state as phosphorite, which is used extensively as a fertilizer. Calcium phosphate is also an important constituent of bones and the seeds of plants.

A very interesting occurrence of phosphorus is pyromorphite (cf. page 182), isomorphous with apatite, vanadinite, and mimetite.

*Properties.*—Phosphorus exists in four allotropic forms:

- (a) As ordinary or colorless phosphorus.
- (b) As red, crystalline phosphorus.
- (c) As bright red phosphorus.
- (d) As black, crystalline phosphorus.

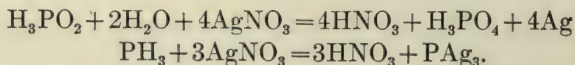
Ordinary phosphorus is poisonous, is colorless when pure (it becomes yellow on exposure to the light, and is coated with a layer of red phosphorus), melts at 44° C., and ignites at 60° C. in the air, so that it must be kept covered with water, in which it is insoluble. It is readily soluble in carbon disulphide, and slightly soluble in ether. It is easily oxidized by nitric acid to phosphoric acid:



The colorless phosphorus, but not the red modification, is oxidized to hypophosphorous and phosphorous acids by exposure to moist air. This causes the characteristic phosphorous odor, and, in the dark, a pale green luminescence. If phosphorus vapors, or phosphine, are allowed to act upon moist silver nitrate paper, the latter is blackened, on account of the formation of silver phosphide and metallic silver. The reaction probably takes place in this way: First, the phosphorus reacts with water to form phosphine and hypophosphorous acid.



which then react with the silver nitrate:




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\* Phosphorus and water by themselves do not react in accordance with this reaction, but it seems probable that they do in the presence of silver nitrate.

This exceedingly sensitive reaction for *colorless* phosphorus was discovered by Scheuer.\* It is a decisive test only when no other substance is present, such as  $\text{H}_2\text{S}$ ,  $\text{AsH}_3$ ,  $\text{SbH}_3$ , formaldehyde or formic acid, which is capable of reacting with silver nitrate.

*Red phosphorus* is crystalline (hexagonal, rhombohedral), and is formed by heating ordinary phosphorus to about  $250^\circ\text{C}$ . out of contact with the air. It is not poisonous, is insoluble in carbon disulphide, and does not ignite until heated to  $256^\circ\text{C}$ . It is non-luminous in the dark, does not oxidize in the air, but is readily oxidized by nitric acid to phosphoric acid.

*Light-red phosphorus* is obtained, according to Schenk,† by heating a solution of white phosphorus in phosphorus tribromide for hours with a return-flow condenser. The phosphorus which then separates is of a light-red color, is not poisonous, but enters into reaction so readily that it is easily distinguished from red phosphorus. It dissolves in concentrated potassium or sodium hydroxide with a stormy evolution of phosphine, the reaction taking place even more readily than with white phosphorus. When covered with ammonia, it blackens.

*Black phosphorus* is obtained when red phosphorus and lead are heated together in a sealed tube to a red heat and the mass treated with dilute nitric acid after it is cold; the lead dissolves and leaves the phosphorus as black phosphorus. By heating to  $360^\circ\text{C}$ . it is changed to ordinary phosphorus again.

Phosphorus is found in a great many organic substances. In order to detect its presence, the compound is heated in a sealed tube with fuming nitric acid, which destroys the organic matter and oxidizes the phosphorus to phosphoric acid (detected by any of the above reactions).

Arsenious, arsenic, and chromic acids, which also belong to this group, have already been described on pages 208, 214 and 99.

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\* Ann. Chem. Phys., 112, 214 (1859).

† Ber., 36, 979 (1903).

**Mitscherlich Test for White, Poisonous Phosphorus.\***

This sensitive test is based upon the luminescence of white phosphorus when exposed to moist air in the dark. It is used to detect phosphorus in cases of poisoning.

*Procedure.*—The food residues, or even the finely-cut pieces of the body, are placed in the liter flask *K* (Fig. 24) and enough

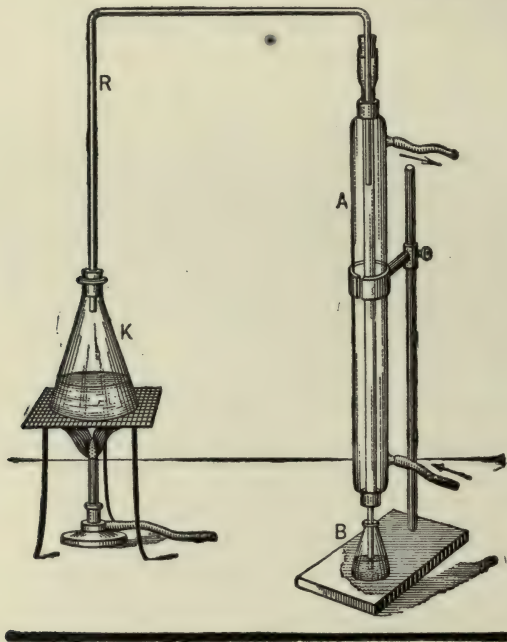


FIG. 24.

water is added to form a thin paste. Then, while shaking, tartaric acid is added to slightly acid reaction, in order to combine with any ammonia present. The tube *R* is then connected with the flask and the contents of the latter are heated to boiling. This operation is carried out in a dark room. As the vapors condense in the tube *A*, a greenish luminous zone is visible even when but a few milligrams of phosphorus are present. If larger

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\* J. pr. Chem., 66, 238 (1855).



quantities of phosphorus are at hand, the distillate in the flask *B* contains tiny globules of phosphorus which, by gently heating and rotating the liquid, can be made to collect into a larger drop; the aqueous solution also contains phosphorous acid which can be detected by the method of Blondlot-Dusart (see below).

If, therefore, the luminosity is apparent during the distillation in the dark, then the presence of white phosphorus is probable but not certain, because phosphorus subsulphide,  $P_4S_3$ , often used as a substitute for phosphorus in the manufacture of matches, will often cause luminescence in the Mitscherlich apparatus,\* especially if a little zinc oxide is added to the liquid in *K* to combine with  $H_2S$ , which tends to prevent the luminescence.

If the luminescence is not apparent, it is not certain that white phosphorus is absent; traces of ammonia, hydrogen sulphide, alcohol, ethereal oils and unsaturated hydrocarbons, interfere with the test. In such cases it is advisable not to stop distilling too soon, as it often happens that the interfering substances will distil over and then the luminescence will appear. In case no luminescence is noticed, the distillate is examined. A part of it is treated with strong chlorine water and evaporated to small volume on the water-bath and then tested for phosphoric acid. Cf. pages 365 and 366.

### Detection of Phosphorus and Phosphorous Acid according to Blondlot-Dusart.†

This beautiful method is based upon Dusart's observation that hydrogen containing phosphine, when allowed to flow from a tube provided with a platinum tip, will burn with a flame having

---

\* I. Mai and F. Schaffer, Ber., 1903, 870; L. Vignon, Bull. soc. chem. [3], 33, 805 (1905), and Schenk and Scharff, Ber., 1906, 1522. The author wishes to state that all commercial preparations of  $P_4S_3$  do not show luminescence in the Mitscherlich apparatus. Thus a sample from Kahlbaum did not show the slightest luminescence by boiling with water or with concentrated salt solution. It was very pure and contained 55.82 per cent. P and 44.14 per cent. S.

† L. Dusart, Compt. rend., 43, 1126 (1856), and Blondlot, J. pharm. chim. [3] 40, 25 (1854).

an emerald green core. The green color is particularly apparent upon holding a cold porcelain dish in the flame.

Since phosphorus, phosphorous acid and hypophosphorous acid (not phosphoric acid) are easily reduced to phosphine by zinc and dilute sulphuric acid, it is merely necessary to pass the evolved gas through a tube with a platinum tip, and light it when the air is all expelled; the merest trace of phosphorus is recognized by the green color.

Inasmuch as organic substances can prevent the appearance of the green flame, the phosphorus is first separated from it as

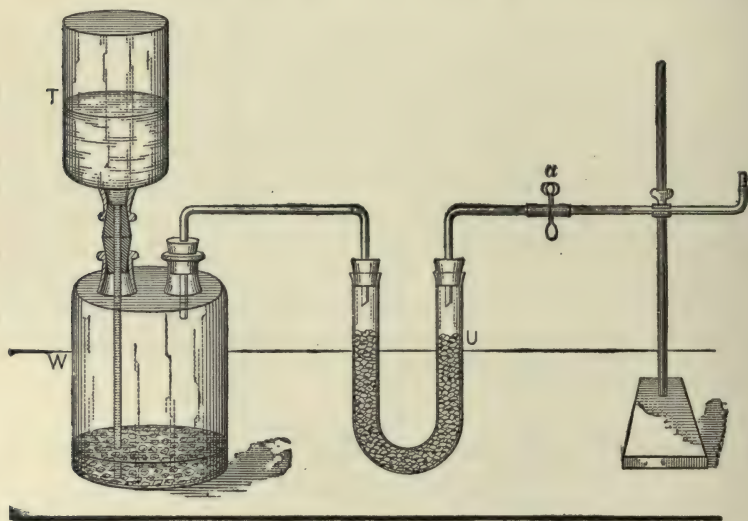


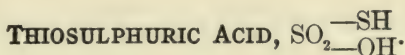
FIG. 25.

follows: The solution containing the phosphorus, or the distillate obtained by the Mitscherlich test, is placed in a gas-evolution flask, zinc (free from phosphorus) and dilute sulphuric acid (1:7) are added, and the evolved gas is passed into a neutral solution of silver nitrate; a black precipitate of silver phosphide is obtained, which, if hydrogen sulphide was present, may contain silver sulphide. This precipitate is filtered off, washed well with water, and placed in the Blondlot apparatus (Fig. 25). In the 500 c.c. Woulfe bottle, *W*, hydrogen is generated by means of zinc free from phosphorus and dilute sulphuric acid (1:7).

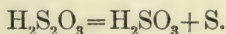
After the air is entirely expelled from the apparatus, the pinch-cock *a* is closed, causing the acid to rise into the reservoir *T* (a bottle with the bottom cut off). The cock *a* is now opened wide enough to permit a steady stream of hydrogen to pass out from the delivery tube, which is made of potash-glass and is provided with a platinum tip.\* The flame from the lighted gas should not be too large.

If the flame shows no green luminescence in the dark when a porcelain dish is introduced, then the hydrogen gas is free from phosphorus and can be used for the test. The black silver precipitate is placed in *T* and rinsed into the bottle *W*. If the precipitate contained phosphorus, the core of the flame becomes green, particularly noticeable upon holding a porcelain dish in it. Any hydrogen sulphide evolved collects in the U-tube, *U*, which contains pumice wet with concentrated caustic potash solution.

Since both the Mitscherlich and the Blondlot-Dusart tests give indications not only of white phosphorus, but also of phosphorus subsulphide, it was desirable to have a test to serve for the identification of white phosphorus with certainty even when the sulphide is also present. For this purpose, R. Schenk and E. Scharff † make use of the property that white phosphorus has of ionizing the atmosphere, a property which is not common to the sulphide. They use the Elster-Geitel apparatus for this purpose. For details of the test the original paper must be consulted.



This very unstable acid is soon decomposed, even in dilute aqueous solution, into sulphurous acid and sulphur:



If the aqueous solution of a thiosulphate is treated with dilute hydrochloric or sulphuric acid, the solution remains clear for a short time; but it soon becomes turbid, owing to the deposition of sul-

\* A small blowpipe tip can be used here or, still better, a cylinder made by rolling together some platinum foil.

† R. Schenk and E. Scharff, Ber., 1906, 1522.

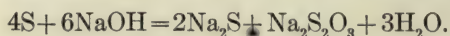


phur, which in this case (unlike most precipitated sulphur) appears yellow.

The salts of thiosulphuric acid, the thiosulphates, are much more stable than the free acid.

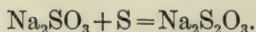
### Formation of Thiosulphates.

1. By boiling sulphur with an alkali or alkaline-earth hydroxide:

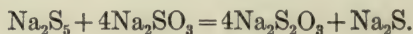


This reaction is analogous to the action of the halogens or of phosphorus upon hydroxides, forming chloride and hypochlorite, phosphide (phosphine), and hypophosphite, etc. (cf. pages 285 and 335).

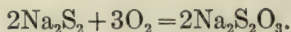
2. By boiling sulphites with sulphur:



3. By treating alkali polysulphides with alkali sulphite in the cold:



4. By the oxidation of polysulphides:



This last reaction takes place on boiling the solution of polysulphide in the air, or very slowly on standing. Yellow ammonium polysulphide is changed, on standing in the air, into ammonium thiosulphate with deposition of sulphur.

The sulphites can be kept well in aqueous solutions provided they are not subjected to the action of carbon dioxide. They are gradually decomposed by the latter, with separation of sulphur.

The most important commercial thiosulphate is the sodium salt  $Na_2S_2O_3 \cdot 5H_2O$ , the well-known "hypo" of photographers.

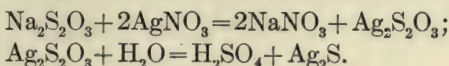
*Solubility.*—The thiosulphates of the alkalis are readily soluble in water, the remaining ones are difficultly soluble; many of them dissolve in an excess of sodium thiosulphate, forming complex salts.

## REACTIONS IN THE WET WAY.

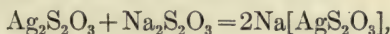
A solution of sodium thiosulphate should be used.

1. **Sulphuric Acid**.—Both dilute and concentrated sulphuric acid decompose thiosulphates, with deposition of yellow sulphur.

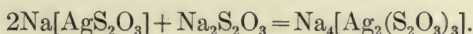
2. **Silver Nitrate** produces a white precipitate, which rapidly becomes yellow, brown, and finally black, owing to the formation of silver sulphide:



Silver thiosulphate is soluble in an excess of the reagent. Difficultly soluble  $\text{Na}[\text{AgS}_2\text{O}_3]$  is at first formed,



which combines with more thiosulphate, forming a soluble complex salt:



But by boiling the solution, silver sulphide is precipitated:



Many other metals behave like silver, especially those of the hydrogen sulphide group. Thus copper, mercurous, and tin salts are precipitated as sulphides by boiling the acid solutions with sodium thiosulphate.†

3. **Barium Chloride** in excess produces a white, crystalline precipitate of barium thiosulphate,‡ difficultly soluble in cold water (480 parts of water at 18° C. dissolve one part of  $\text{BaS}_2\text{O}_3$ ), but fairly soluble in hot water.

4. **Strontium Chloride** produces a white, crystalline precipitate, but only in very concentrated solutions (3.7 parts of water at 18° C. dissolve one part of  $\text{SrS}_2\text{O}_3$ ).

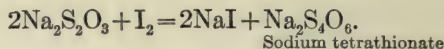
\* When  $\text{AgCl}$  is dissolved in sodium thiosulphate solution, no precipitation of  $\text{Ag}_2\text{S}$  takes place in the cold, and on heating only very slowly if a large excess of sodium thiosulphate is present. If the solution of  $\text{AgCl}$  in  $\text{Na}_2\text{S}_2\text{O}_3$  is diluted largely, then an abundant precipitate of  $\text{Ag}_2\text{S}$  is produced on boiling.

† Z. anorg. Chem., 28, 223 (1902).

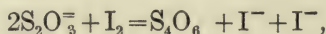
‡ Rubbing the sides of the test-tube hastens the formation of this precipitate.

5. **Lead Acetate** precipitates white lead thiosulphate, soluble in an excess of the alkali thiosulphate. On boiling the solution a voluminous precipitate, consisting of lead sulphate and lead sulphide, is formed.

6. **Iodine Solution** is decolorized by solution of thiosulphates:

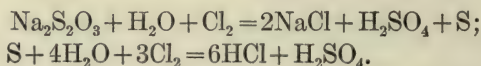


This reaction is explained, according to the dissociation theory, as follows:



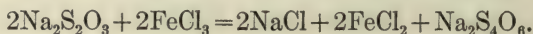
The negative anions,  $\text{S}_2\text{O}_3$ , transfer half of their electric charge to the undissociated, and consequently uncharged, iodine atoms; which changes the latter to ions, while the two half-discharged  $\text{S}_2\text{O}_3$  ions unite, forming bivalent  $\text{S}_4\text{O}_6$  ions.

Chlorine and bromine in excess\* act quite differently upon thiosulphates. If chlorine (or bromine) is conducted into a solution of sodium thiosulphate, a considerable precipitation of sulphur takes place, which, upon further action of the halogen, disappears:



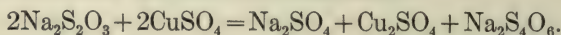
Other weak oxidizing agents act in the same way as iodine. Thus,

7. **Ferric Chloride** produces, in solutions of sodium thiosulphate, at first a dark-violet coloration (perhaps ferric thiosulphate), which disappears after some time, leaving a colorless solution containing ferrous chloride and sodium tetrathionate:

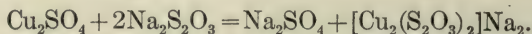


Similarly,

8. **Cupric Salts** are reduced to colorless cuprous compounds, with the formation of sodium tetrathionate:



The unstable cuprous sulphate immediately acts upon more thiosulphate, forming sodium cuprous thiosulphate:




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\* Cf. p. 298.



If the colorless solution of the cuprous salt is treated with caustic potash solution, yellow cuprous hydroxide is in some cases immediately formed, in other cases only on standing or on warming. The precipitate becomes darker colored on being boiled.

If the solution is acidified and boiled, black cuprous sulphide is precipitated.

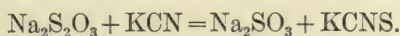
The colorless solution of the cuprous salt gives also a white (usually almost a light red) precipitate with potassium ferrocyanide or cuprous ferrocyanide.

9. **Nascent Hydrogen** (zinc and hydrochloric acid) causes the evolution of hydrogen sulphide.

10. **Zinc Salts** produce no precipitate (difference from sulphides).

11. **Zinc Sulphate and Sodium Nitroprusside** produce no red coloration (difference from sulphites).

12. **Potassium Cyanide**.—Boiling a solution of a thiosulphate with potassium cyanide and caustic soda transforms the thiosulphate into sulphite and the cyanide into sulphocyanate;



On acidifying the solution with hydrochloric acid and adding ferric chloride, the blood-red color of ferric sulphocyanate is obtained (difference from sulphites).

### Detection of Sulphurous and Thiosulphuric Acids in the Presence of Hydrogen Sulphide.

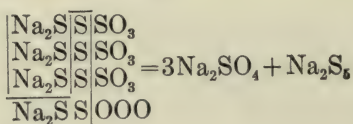
The three acids are assumed to be present together in solution in the form of their alkali salts. The fairly concentrated solution is treated with zinc sulphate, and the zinc sulphide formed is filtered off. The filtrate is treated with strontium nitrate solution and allowed to stand over night, when the strontium sulphite is filtered off and washed with a little cold water. If the strontium sulphite is treated on the filter with dilute hydrochloric acid, sulphurous acid goes into solution, which can be detected by its property of decolorizing an iodine solution. In the filtrate from the strontium sulphite, the thiosulphate remains; it can be detected by acidifying with hydrochloric acid and warming, when sulphur will be deposited.

*Solubility of Sulphites and Thiosulphates of the Alkaline\*  
Earths in Water.*

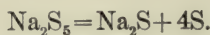
	Sulphite.	Thiosulphate.
Calcium.....	1:800	1:2
Strontium.....	1:30000	1:3.7
Barium .....	1:46000	1:480

REACTIONS IN THE DRY WAY.

The thiosulphites of the alkalies, on being heated out of contact with the air, are changed into sulphate and polysulphide, and the latter into sulphide and sulphur:



and



If this reaction is performed in a closed tube, a sublimate of sulphur is obtained (difference from sulphites); and the residue yields hydrogen sulphide if treated with acid.

## GROUP V.

**Silver Nitrate** produces no precipitate in acid or neutral solutions.

**Barium Chloride**, also, causes no precipitation.

## NITRIC ACID, $\text{HNO}_3$ .

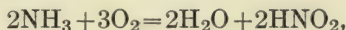
*Occurrence.*—Nitric acid is found in the form of nitrates in small amounts almost everywhere in nature; thus the ammonium salt is found in the atmosphere and in soils; the calcium salt is found in old masonry; while the sodium salt is found in rainless localities, particularly in Chili (Chili saltpetre).

Nitric acid is the final product of the oxidation of ammonia; it is found wherever nitrogenous organic substances have been subjected to decay, forming ammonia. With the help of micro-organisms

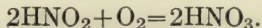
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\* Autenrieth and Windaus, Z. anal. Chem., 1898, p. 295.

(*Monas nitrificans*, according to Winogradsky) the ammonia is changed first to nitrous acid,



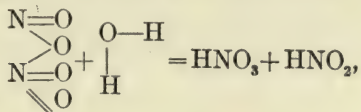
which, by further oxidation, is changed to nitric acid:



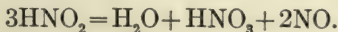
*Properties.*—Pure nitric acid is a colorless liquid, with a specific gravity of 1.54 at 20° C. At 86° C. it begins to boil, with decomposition, giving off its anhydride, which suffers further decomposition into nitrogen peroxide,  $\text{NO}_2$  (brown fumes), and oxygen. By the constant loss of  $\text{N}_2\text{O}_5$ , the nitric acid becomes more and more dilute and the boiling-point constantly rises, until at 120.5° C. it remains constant; when nitric acid of specific gravity 1.414 distils over, forming a 68 per cent. acid. If a more dilute acid is subjected to distillation, water is at first given off, the boiling-point constantly rising until 120.5° C. is reached, when a 68 per cent. acid again distils unchanged.

Red, fuming nitric acid is obtained by conducting  $\text{NO}_2$  into the colorless, concentrated acid. In its most concentrated condition it possesses a specific gravity of 1.55.

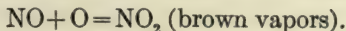
If the fuming acid is treated with water, it is colored green, and vapors of nitric oxide are given off, which are colored brown on coming in contact with the air. The dissolved  $\text{NO}_2$  (or, better,  $\text{N}_2\text{O}_4$ ), being a mixed anhydride is changed into nitric and nitrous acids,



and the nitrous acid, owing to the heat of reaction, is partly changed into nitric acid, with evolution of nitric oxide,



and



Nitric acid is a strong oxidizing agent (cf. page 4). It is monobasic, and, next to the halogen acids, is the strongest acid. It forms



stable salts, which are all soluble in water; but a few of them are changed by water into basic salts (cf. bismuth and mercuric salts), insoluble in water, but soluble in nitric acid.

#### REACTIONS IN THE WET WAY.

As nitric acid does not form insoluble salts, it cannot be detected by means of precipitation; its characteristic reactions depend upon its oxidizing action. Great care must be exercised before deciding whether this acid is present, for other oxidizing substances give similar (in some cases the same) reactions.

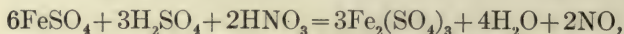
1. **Dilute Sulphuric Acid** gives no reaction (difference from nitrous acid).

2. **Concentrated Sulphuric Acid** when heated with any nitrate causes evolution of yellow to brown vapors of  $\text{NO}_2$ , with a characteristic penetrating odor.

3. **Silver Nitrate** and **Barium Chloride** cause no precipitation.

4. **Ferrous Salts** are oxidized by nitric acid, which is itself reduced to nitric oxide,  $\text{NO}$ . If the reaction takes place in the cold, the latter combines with the excess of ferrous salt, forming a dark-brown, very unstable compound,  $\text{FeX}_2 \cdot \text{NO}$ . This compound is decomposed, on warming, into ferrous salt and nitric oxide (which escapes) the brown color disappearing. If the amount of nitric acid present is more than sufficient to completely oxidize the ferrous salt to ferric salt, the brown color will only appear as representing a transient intermediate product; for ferric salts do not unite with nitric oxide.

The oxidation takes place according to the following reaction,



and is best carried out in the following manner:

A little of the substance to be tested for nitric acid is placed in a test-tube and dissolved in as little water as possible; a cold saturated solution of ferrous sulphate is added, the two solutions mixed, and the sulphuric acid carefully poured down the sides of the tube. If nitric acid is present, the contact zone will be colored distinctly brown.

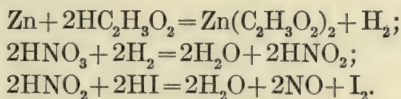
Nitrous acid gives the same reaction, with the difference that it takes place without the addition of concentrated sulphuric acid.

5. **Indigo Solution** is decolorized by warming with nitric acid (as well as by other oxidizing agents).

6. **Potassium Iodide** is not decomposed by pure, dilute nitric acid (difference from nitrous acid).

If to the solution of a nitrate we add potassium iodide, a few drops of an acid (best acetic acid), and a little zinc, the nitric acid is reduced to nitrous acid, which then reacts with hydriodic acid so that the solution becomes yellow on account of the separation of iodine. By shaking the solution with carbon disulphide, the latter will be colored reddish violet,\* or the iodine may be detected by adding a little starch paste.

The reactions which take place may be represented by the following equations:



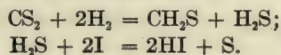
7. **Diphenylamine Reaction** (the Lunge test †).—The reagent is prepared by dissolving 0.5 gm. of diphenylamine in 100 c.c. of pure concentrated sulphuric acid and adding 20 c.c. of water.

*Procedure.*—A few cubic centimeters of the diphenylamine solution are placed in a test-tube and carefully covered with the solution to be tested for nitric acid. If the latter is present, there is formed at the zone of contact between the two liquids a ring of a beautiful blue color.

This very sensitive reaction is, unfortunately, also caused by nitrous, chloric, and selenic acids, ferric chloride, and many other oxidizing agents.

In the absence of ferric and selenic salts, it is useful for detecting

\* If it is desired to detect the iodine by means of carbon disulphide, the latter *under no circumstances* should be added before the zinc has been allowed to act upon the acid solution of the nitrate and potassium iodide. In such a case, there will often be no separation of iodine, because the nascent hydrogen is used up reducing the carbon disulphide to thioformaldehyde and hydrogen sulphide, and the latter reacts with any iodine which may be formed, changing it back to hydriodic acid:



† Lunge, *Z. angew. Chemie*, 1894, Heft 12.

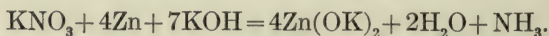
the presence of small amounts of nitrogen acids in sulphuric acid. In this case the concentrated sulphuric acid which is to be tested is first poured into the test-tube, and the specifically lighter diphenylamine solution is then poured on top. If one c.c. of an acid containing only  $\frac{1}{20}$  milligram of nitrogen in a liter is used, the reaction will cause a noticeable coloration.

**8. Brucine Reaction.**—The reagent \* is prepared by dissolving 0.2 gm. of brucine in 100 c.c. of pure concentrated sulphuric acid.

*Procedure.*—The solution to be tested for nitric acid is mixed with three times its volume of pure concentrated sulphuric acid, and one c.c. of brucine solution is added. If nitric acid is present, a red coloration quickly appears, which quickly changes to orange, then slowly to lemon or gold yellow, and finally becomes greenish yellow. Nitrous acid does not give this reaction provided it is present as "nitrose," i.e., dissolved in concentrated sulphuric acid. Aqueous solutions of nitrites always yield a small amount of nitric acid when acidified with sulphuric acid, and consequently give the brucine reaction.

**9. Zinc in Alkaline Solution** reduces nitric acid to ammonia.

If a nitrate solution is boiled with zinc dust and an alkali, a considerable evolution of ammonia takes place:



Devarda's alloy reacts much more quickly with a drop of caustic soda.

This reaction is particularly suited for the detection of nitric acid in the presence of chloric acid (cf. page 387).

### Detection of Nitric Acid in the Presence of Nitrous Acid.

With the exception of the Lunge-Lwoff method, there is no absolutely reliable qualitative test for the detection of traces of nitric acid in the presence of large amounts of nitrous acid in aqueous solution. A number of methods have been proposed which depend upon the destruction of the nitrous acid by diazotizing, but they all yield only approximate results; because, in order to destroy the nitrous acid, it is necessary first to set the acid itself free by the addition of another acid, which always causes a part of the nitrous

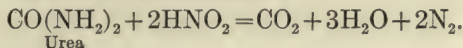
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\* Lunge, Z. angew. Chemie, 1894, Heft 12.

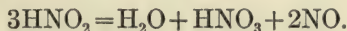


acid to be changed to nitric acid; so that the latter will be detected even when no nitric acid was originally present.

Large amounts of nitric acid in the presence of nitrous acid may be detected by the method proposed by Piccini,\* in which a concentrated solution containing salts of both acids is treated with a concentrated solution of urea, and then covered (by means of a pipette) with dilute sulphuric acid. A lively evolution of nitrogen ensues, which ceases in a few minutes:



This reaction, however, does not take place quickly enough to prevent traces of nitric acid being formed according to the following equation:



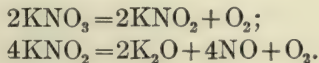
The odor of nitrous fumes is always perceptible in the escaping nitrogen,† which can also usually be detected by means of iodostarch paper. The nitric acid which remains in the solution can be detected by means of the diphenylamine reaction.

The nitrous acid may also be destroyed by boiling an alkaline nitrite solution with neutral ammonium chloride; but traces of nitric acid are always in evidence at the same time.‡

If the diphenylamine reaction gives a very intense coloration after the destruction of the nitrous acid by means of urea, the presence of nitric acid in the original compound is assured; but if the reaction shows that only a trace of nitric acid is present, it is probably due simply to small amounts of nitric acid formed by the destruction of the nitrous acid.

#### REACTIONS IN THE DRY WAY.

By the ignition of nitrates of the alkalies, they are changed into nitrites with loss of oxygen, and the latter are decomposed on stronger ignition into oxide:



\* Z. anal. Chem., 19, 354.

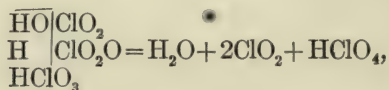
† Even at 0° and in an atmosphere of carbon dioxide.

‡ By evaporating with ammonium carbonate solution the decomposition scarcely takes place at all.

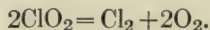
All nitrates deflagrate on being heated on charcoal; *i.e.*, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

### CHLORIC ACID, $\text{HClO}_3$ .

Free chloric acid is extremely unstable, and is decomposed, at  $40^\circ \text{C}$ ., into perchloric acid with loss of chlorine and oxygen:



and



The salts of the monobasic chloric acid, the chlorates, are quite stable, and are all soluble in water. They are formed by conducting chlorine into hot alkali hydroxide solutions, which are not too concentrated.\*

### REACTIONS IN THE WET WAY.

1. **Dilute Sulphuric Acid** sets free chloric acid from chlorates, which, as above stated, is gradually decomposed, with loss of chlorine and oxygen, into perchloric acid. The solution, therefore, acts as a bleaching agent,† particularly on warming. The neutral salts do not bleach (difference from hypochlorites).

2. **Concentrated Sulphuric Acid** decomposes all chlorates, setting free greenish-yellow chlorine dioxide gas, which violently explodes on warming:



3. **Silver Nitrate** and **Barium Chloride** do not cause precipitation.

\* F. Winteler, *Z. anorg. Chem.*, **33**, 188 (1902).

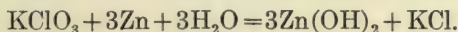
† The solution turns iodo-starch blue. If the solution is very dilute this test is not obtained; the blue color is obtained more quickly in proportion to the quantities of sulphuric and chloric acids present.

4. **Nascent Hydrogen** reduces chlorates to chlorites in acid, alkaline, and neutral solutions.

The reduction in acid solution is effected by means of zinc and dilute sulphuric acid, or by means of sulphurous acid:

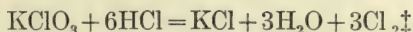


The reduction in alkaline or neutral \* solution is brought about by boiling the solution with zinc dust, or, better, by means of Devarda's alloy (cf. page 8):

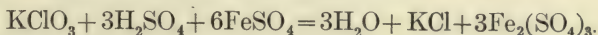


The residue of zinc dust (or copper, if the alloy is used) is filtered off, the solution acidified with nitric acid,† and silver nitrate added, when the characteristic, curdy precipitate of silver chloride is formed.

5. **Concentrated Hydrochloric Acid** decomposes all chlorates, with evolution of chlorine:



6. **Ferrous Salts**.—By boiling chlorates with ferrous salts in the presence of dilute sulphuric acid, the chlorate is quickly reduced to chloride (difference from perchloric acid):



7. **Diphenylamine** reacts the same as with nitric acid.

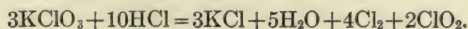
### Detection of Hydrochloric, Nitric, and Chloric Acids in the Presence of One Another.

I. First, the presence of hydrochloric acid is confirmed by precipitating a part of the solution with silver nitrate; a white precipi-

\* The reaction takes place very slowly in neutral solutions.

† On acidifying with nitric acid a heavy precipitate of  $\text{Zn}(\text{OH})_2$  is obtained which dissolves in more nitric acid.

‡ This equation is not correct, for some  $\text{ClO}_2$  is always mixed with the  $\text{Cl}_2$ . The following equation expresses this:





tate of silver chloride shows the presence of hydrochloric acid. The remainder of the solution is treated with silver sulphate solution until no further precipitation of silver chloride takes place, and the precipitate is filtered off.

The filtrate is boiled with a little caustic potash (in order to expel any ammonia from ammonium salts which may be present), treated with zinc dust (or Devarda's alloy), and again boiled; if nitric acid is present, ammonia will be given off. The residue is filtered off, the filtrate acidified with nitric acid and treated with silver nitrate. If a precipitate of silver chloride is now obtained, chloric acid was originally present.

II. Or, a small part of the solution is tested for hydrochloric acid by adding silver nitrate in excess, the precipitate is filtered off, the filtrate treated with sulphurous acid, and again tested with silver nitrate, when a precipitate of silver chloride shows the presence of chloric acid.

A second portion of the solution is tested, as above, for nitric acid.

#### REACTIONS IN THE DRY WAY.

On ignition, all chlorates are decomposed, forming a chloride, with loss of oxygen. By heating on charcoal, deflagration takes place.

#### PERCHLORIC ACID, $\text{HClO}_4$ .

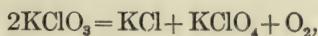
Free perchloric acid is obtained by the distillation of potassium perchlorate with concentrated sulphuric acid. In this way the solid, crystalline hydrate  $\text{HClO}_4 + \text{H}_2\text{O}$  is obtained, which, on heating to  $110^\circ \text{C}$ ., is broken up; the anhydrous liquid acid distils off first and fumes strongly in the air, while the oily hydrate  $\text{HClO}_4 + 2\text{H}_2\text{O}$  remains behind until the temperature reaches  $203^\circ \text{C}$ ., when it also distils.

The free acid is very dangerous, and often explodes spontaneously. In aqueous solution, however, it can be kept without danger.

The salts of this monobasic acid are remarkably stable.

The potassium salt is obtained from potassium chlorate. On melting the latter compound, at first a lively stream of oxygen is given off which, however, soon lessens. The melt quickly be-

comes viscous, and consists of potassium chloride and potassium perchlorate,



and the latter may be separated from the much more soluble potassium chloride by recrystallization.

*Solubility*.—All perchlorates are soluble in water.

#### REACTIONS IN THE WET WAY.

Perchloric acid is not attacked by concentrated sulphuric acid, nor reduced to chloride by zinc dust, Devarda's alloy, sulphurous acid, or acid solutions of ferrous salts.

**Potassium Salts** precipitate the relatively insoluble, white, crystalline  $\text{KClO}_4$  (cf. page 50).

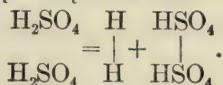
**Silver Nitrate and Barium Chloride** produce no precipitation.

#### REACTIONS IN THE DRY WAY.

The perchlorates deflagrate on being heated on charcoal; by fusing they lose oxygen, leaving chloride behind, which when dissolved in water gives all the reactions for hydrochloric acid.

#### PERSULPHURIC ACID, $\text{H}_2\text{S}_2\text{O}_8$ .

Pure persulphuric acid itself has never been isolated, its solution in sulphuric acid alone being known. It was first prepared by M. Marshall,\* who electrolyzed fairly dilute sulphuric acid, keeping it very cold. In this process the  $\text{HSO}_4$  of sulphuric acid unite at the anode, forming persulphuric acid:



The preparation of ammonium persulphate, from which all other persulphates are made, is entirely analogous.

The most important salts of persulphuric acid are those of ammonium, potassium, and barium.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is readily soluble in water, and forms monoclinic crystals;  $\text{K}_2\text{S}_2\text{O}_8$  is difficultly soluble in cold water, but much more soluble in hot water, from which

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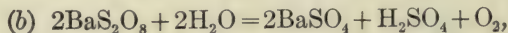
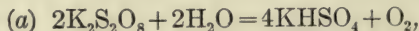
\* J. Chem. Soc., 59, 771.

solution it is obtained by rapid cooling in the form of long crystals;  $\text{BaS}_2\text{O}_8 + 4\text{H}_2\text{O}$  is made by rubbing ammonium persulphate with barium hydroxide, and is fairly soluble in water.

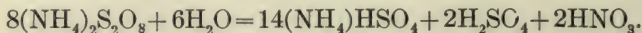
#### REACTIONS.

A solution of ammonium persulphate may be used.

1. All persulphates are decomposed in aqueous solution (slowly in the cold, but more quickly on warming), forming sulphate, free sulphuric acid, and oxygen:



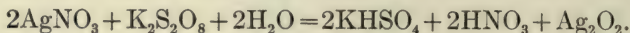
A large proportion of the oxygen escapes as ozone, which can be detected by its odor, or by its property of turning iodo-starch paper blue. A dilute solution of ammonium persulphate decomposes slowly at  $20^\circ \text{C}$ ., without evolution of oxygen, part of the nitrogen being oxidized to nitric acid:



2. **Dilute Sulphuric Acid** acts the same as water.

3. **Concentrated Sulphuric Acid.**—If a solid persulphate is dissolved in concentrated sulphuric acid at  $0^\circ \text{C}$ ., a liquid is obtained which possesses very strong oxidizing properties. The mixture is known as Caro's acid.\* For further particulars concerning this acid, the student is referred to A. Baeyer's interesting work.†

4. **Silver Nitrate** precipitates black silver peroxide:



If, however, the concentrated solution of ammonium persulphate is treated with ammonia and a very little silver nitrate, a lively evolution of nitrogen takes place, and the solution becomes heated to boiling. Silver peroxide is formed first, and oxidizes the ammonia to water, setting free nitrogen (Catalysis).‡

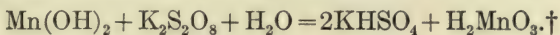
\* Z. angew. Chem., 1898, p. 845.

† Ber., 34, 853 (1901).

‡ Z. phys. Chem., 37, p. 255 (1901).



5. **Manganese, Cobalt, Nickel, and Lead Salts** are oxidized in the presence of alkali\* to black peroxides:



In this last reaction persulphuric acid reacts exactly similarly to hydrogen peroxide. It may be distinguished, however, from the latter by the fact that it does not decolorize a solution of potassium permanganate, does not produce a yellow coloration with titanium sulphate, and does not react with chromic acid to form chromium peroxide (cf. page 53). Ferrous salts are readily oxidized to ferric salts, and cerous salts are changed to yellow ceric salts by persulphates, but the latter are not decolorized by an excess of the persulphate, while they are by hydrogen peroxide.

6. **Barium Chloride** does not give a precipitate immediately in a freshly-prepared cold solution of a persulphate; but, on standing some time, or on boiling, insoluble barium sulphate is precipitated.

## GROUP VI.

**Silver Nitrate** produces no precipitate.

**Barium Chloride** produces a white precipitate, almost insoluble in acids.

## SULPHURIC ACID, $\text{H}_2\text{SO}_4$ .

Pure sulphuric acid at ordinary temperatures is a colorless, oily liquid of specific gravity 1.8384; at low temperatures it is a solid. If the acid is subjected to distillation, it is always partially decomposed; heavy, white vapors of  $\text{SO}_3$  are given off first, and at  $338^\circ \text{C}$ . a 98 per cent. acid distils over. Ordinary commercial sulphuric acid has a specific gravity of 1.83–1.84, and contains 93–96 per cent.  $\text{H}_2\text{SO}_4$ . It often contains lead sulphate, selenic acid, platinum, palladium, arsenious acid, the nitrogen acids, and small amounts of organic matter (whereby it is often colored brown) as impurities.

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\* Manganese and lead salts are precipitated quantitatively from neutral and slightly acid solutions by alkali persulphates, cobalt incompletely from neutral solutions and not at all from acid ones, and nickel only in the presence of alkali. Hydrogen peroxide produces precipitates of peroxides in all these solutions only in the presence of alkali.

† Cf. page 140.

Concentrated sulphuric acid is very hygroscopic, and is used, therefore, for drying gases, etc.

The anhydride of sulphuric acid,  $\text{SO}_3$ , dissolves in concentrated sulphuric acid, forming pyrosulphuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ , which is solid at ordinary temperatures, melts at  $35^\circ \text{C}$ ., and loses  $\text{SO}_3$  at higher temperatures. It fumes strongly, and is called, therefore, fuming sulphuric acid. Sulphuric acid is dibasic and forms both neutral and acid salts.

*Solubility.*—Most sulphates are soluble in water; calcium sulphate is difficultly soluble, strontium and lead sulphates are very difficultly soluble, while barium sulphate is practically insoluble in water. There are also a number of basic sulphates, Hg, Bi, Cr, which are insoluble in water, but are, as a rule, soluble in acid.

#### REACTIONS IN THE WET WAY.

1. **Sulphuric Acid** naturally gives no reaction.
2. **Silver Nitrate** causes no precipitation in dilute solutions, but in concentrated solutions a white crystalline precipitate is formed (100 parts of water dissolve at  $18^\circ \text{C}$ . only 0.58 part of silver sulphate).
3. **Barium Chloride** precipitates, from even the most dilute solutions, white barium sulphate, insoluble in acids.
4. **Lead Acetate** precipitates white lead sulphate, soluble in concentrated sulphuric acid, ammonium acetate, and ammonium tartrate solutions (cf. page 188).

In order to detect the presence of the  $\text{SO}_4$  ion in insoluble sulphates, they are treated with sodium carbonate, whereby insoluble carbonate and soluble sodium sulphate are formed.

Lead sulphate and calcium sulphate are easily decomposed by boiling with sodium carbonate solution, but barium and strontium sulphates are only incompletely decomposed by this treatment; they are much more readily attacked by fusing with four times as much sodium carbonate (cf. page 75).

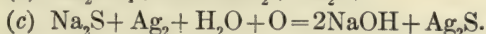
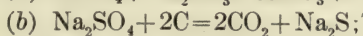
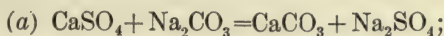
5. **By Nascent Hydrogen** (zinc and acid) the sulphates are not reduced.

## REACTIONS IN THE DRY WAY.

The neutral salts of the alkalies melt with difficulty without being decomposed, while the acid salts of the alkalies readily give off water and  $\text{SO}_3$  (cf. page 94).

The sulphates of the alkaline earths and of lead do not undergo decomposition on ignition; the remaining sulphates are more or less decomposed.

All sulphates are reduced to sodium sulphide when heated with sodium carbonate on charcoal; if the product is placed upon a bright silver coin and moistened, a black stain of silver sulphide results; *e.g.*:

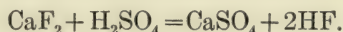


This reaction is called the Hepar reaction.

## HYDROFLUORIC ACID, HF.

*Occurrence.*—Hydrofluoric acid occurs in nature only in the form of fluorides, of which the most important is fluorite,  $\text{CaF}_2$ , crystallizing in the isometric system. It is also found as cryolite,  $(\text{AlF}_6)\text{Na}_3$ , in Greenland, and in many silicates, such as tourmaline, topaz, lepidolite, apophyllite, apatite, etc.

*Preparation.*—Hydrofluoric acid is obtained by decomposing a fluoride with concentrated sulphuric acid in platinum or lead retorts:

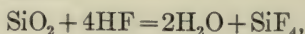


*Properties.*—Hydrofluoric acid at temperatures above  $20^\circ \text{C}$ . is a colorless gas which changes at  $19.4^\circ \text{C}$ . to a mobile, fuming liquid. The vapors possess a penetrating odor and are poisonous. When in contact with the skin it produces painful burns. On heating the concentrated aqueous solution, the gas HF at first distills and then the 36 per cent acid.

Hydrofluoric acid is distinguished from all other acids by its ability to dissolve silicic acid, a property which is utilized technically for etching glass, and in the analytical laboratory for detecting fluorine and silicic acid, as well as for decomposing silicates. On account of this action upon glass the acid must be kept in platinum, wax, or hard rubber, and prepared in platinum or lead vessels.



The action of hydrofluoric acid upon silicic acid takes place according to the equation



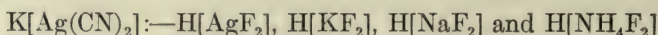
and the velocity of the reaction depends upon the fineness and nature of the material. Thus Mackintosh \* found after one hour's action of an excess of 9 per cent. hydrofluoric acid upon quartz and opal powder that the quartz had lost only 1.56 per cent. of its original weight while the opal had lost 77.28 per cent.

If precipitated and ignited silica is treated with strong hydrofluoric acid, it dissolves almost immediately with hissing and strong evolution of heat, while quartz powder under the same treatment is dissolved only slowly.

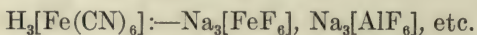
Most silicates, with regard to the ease with which they are attacked by hydrofluoric acid, stand intermediate between the precipitated silica and quartz, although some silicates are attacked more difficultly than is quartz and a few are only slightly acted upon.

Hydrofluoric acid is a weak, monobasic acid having, in common with other weak acids like carbonic acid, acetic acid, etc., the property of turning blue litmus red and Brazil-wood paper yellow. The aqueous solution of an alkali fluoride has a strong alkaline reaction.

The property of forming very stable complex metal-hydrofluoric acids is characteristic of hydrofluoric acid as of hydrocyanic acid:



and corresponding to ferricyanic acid:



Unlike the complex cyanogen compounds, of which the free acids either do not exist at all or represent very unstable compounds, the corresponding fluorine acids are fairly stable. Thus hydroargenticfluoric acid,  $\text{H}[\text{AgF}_2]$  decomposes only on gently heating it, into silver fluoride and hydrofluoric acid, and the corresponding alkali compounds are decomposed only upon ignition; for this reason the latter are suitable for attacking difficultly decomposable silicates, zircon and titanium minerals, etc., which are only partially attacked by free hydrofluoric acid.

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\* Chem. News, 54, 102.

*Solubility.*—The fluorides of the alkalis, of silver, aluminium, tin, and mercury are soluble in water, while those of the alkaline earths, of lead, copper, and zinc, are insoluble, or at least very difficultly soluble.

#### REACTIONS IN THE WET WAY.

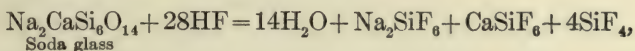
For reactions 1, 2, and 3, powdered calcium fluoride may be used, but for reactions 4, 5, 6, and 7, a solution of sodium fluoride is necessary.

1. **Dilute Sulphuric Acid** causes only a slight reaction.

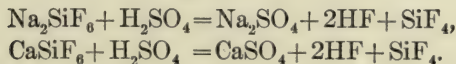
2. **Concentrated Sulphuric Acid** reacts readily on warming, setting free hydrofluoric acid:



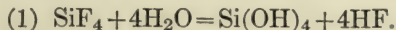
If this reaction is performed in a test-tube, the hydrofluoric acid will attack the glass, forming volatile silicon fluoride and salts of hydrofluosilicic acid; but the latter are decomposed by the concentrated sulphuric acid into sulphate, hydrofluoric acid, and silicon fluoride,



and



The silicon fluoride formed by this reaction is a colorless gas with a penetrating odor, and is decomposed by water, forming gelatinous silicic acid and hydrofluoric acid:

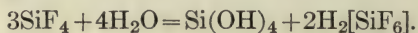


Silicon fluoride, however, readily combines with hydrofluoric acid to form hydrofluosilicic acid:



and the latter compound is not decomposed by water. The whole

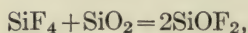
reaction, therefore, which takes place between silicon tetrafluoride and water is expressed by the sum of the two equations, as follows:



If, therefore, a fluoride be heated in a glass test-tube with concentrated sulphuric acid, and the escaping vapors allowed to act upon water, by placing a moist glass tube rod in the tube, the water adhering to the rod will become turbid.

*Remark.*—Although the above test rarely fails when relatively large amounts of fluoride are used, it will not be obtained in the case of certain minerals containing fluorine, such as topaz, tourmaline, etc. The test may fail, furthermore, if the fluoride is mixed with a large excess of that modification of silicic acid which is most readily attacked by hydrofluoric acid. According to Daniel,\* this is due to the formation of a stable oxyfluoride probably of the formula  $\text{SiOF}_2$ .

The silicon tetrafluoride at first formed combines with the excess of amorphous silicic acid present, as follows:



but this reaction will take place only very slowly if at all with quartz powder or with the silica of a silicate such as glass.

A positive result will be obtained invariably when the tetrafluoride test is made in a platinum vessel with a relatively large amount of fluoride and comparatively little amorphous silicic acid or silicate (large amounts of quartz do not influence the reaction); the test will be negative, on the other hand, if made in platinum with no silicic acid, or, strange to say, when only quartz is present with the fluoride. The reason for this different behavior lies in the difficulty with which quartz is attacked by hydrofluoric acid.

Daniel recommends the following method for performing the test:

The substance to be tested for fluorine is mixed with about

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\* Z. anorg. Chem., 38 (1904), p. 299.



three times as much (by volume) ignited quartz powder, and mixed to a paste in a test-tube with concentrated sulphuric acid. The test-tube is then closed with a cork in which one hole has been bored and an opening cut in the side. Through the hole in the cork is passed a glass rod blackened with asphalt paint, and on the bottom of the rod hangs a drop of water suspended; this rod is pushed down until it is only a distance equal to about  $1\frac{1}{2}$  the diameter of the test-tube from the paste in the bottom. The tube and its contents are gently heated over a small flame, and if a fluoride is present a white film of  $\text{Si}(\text{OH})_4$  will be formed in the drop of water and will be shown plainly in contrast to the black rod. In a tube with 1 cm. diameter fluorine equivalent to 1 milligram of calcium fluoride may be detected, while with a tube of only 0.5 cm. diameter as little as 0.1 milligram of calcium fluoride will give the test. When using a tube of small diameter, it is best to add the sulphuric acid through a small capillary pipette to avoid wetting the sides of the tube.

If the substance contains considerable amorphous silica, or when an oxyfluoride, such as topaz, is present, which is hard to decompose with sulphuric acid, the test will fail, and it is then necessary to make use of the etching test.

**3. The Etching Test.**—The substance to be tested for fluoride is placed in a platinum crucible, treated with concentrated sulphuric acid, and the crucible covered with a watch-glass whose convex side is provided with a thin coating of beeswax upon which a few letters have been written. On warming the contents of the crucible, the glass will be etched at the places where the escaping gas comes in contact with it, if a fluoride was originally present. By covering the upper concave side of the watch-glass with a little cold water, the wax coating will not melt during the experiment.

If it is desired to detect the presence of a trace of fluorine, the crucible is allowed to stand covered with the watch-glass for twelve hours and then heated for a few minutes. The presence of only 0.0003 gm. of calcium fluoride is sufficient to give this test, provided a crucible of the right size is used.

If the fluoride contained silica (as in topaz, tourmaline, and other minerals), the etching test will be negative, for even if the fluorine escapes, it will be in the form of silicon fluoride which does not attack glass.

In order to detect small amounts of fluoride in silicates, it is necessary first to transform the fluorine into calcium fluoride and to subject the latter compound to the test.

In order to separate the fluorine as calcium fluoride, the following process is used:

The finely-pulverized silicate is mixed with 6-8 times as much sodium carbonate, fused in a platinum crucible, and the melt treated with water after it is cold. A solution is then obtained in which all of the fluorine is present as sodium fluoride, together with sodium silicate. The silica is removed by adding considerable ammonium carbonate to the solution, warming it slightly, and allowing it to stand twelve hours. After filtering off the silica, the solution is evaporated to a small volume, and a little phenolphthalëin added, which will cause the solution to become reddish. Hydrochloric acid is carefully stirred in until the solution becomes colorless, and it is heated to boiling, when the color will reappear. The solution is again decolorized with hydrochloric acid after it has become cold, and the process repeated until the solution becomes only faintly colored on boiling it.

Calcium chloride solution is now added and the solution again boiled. The precipitate formed consists of calcium carbonate and calcium fluoride; it is filtered off, washed, dried, and ignited in a platinum crucible. The ash is then treated with dilute acetic acid, evaporated to dryness, triturated with water and the undissolved calcium fluoride filtered off. After drying the precipitate and burning the filter, it is ready for the etching test.

4. **Silver Nitrate** causes no precipitation from solutions of soluble fluorides.

5. **Barium Acetate** precipitates barium fluoride soluble in an excess of mineral acid and in ammonium salts. Traces of fluorine present as preservative in foods, liquors. etc., may be detected by adding a little potassium sulphate (about 0.3 gm.) to the solution, heating it to boiling and slowly introducing 10 c.c. of 10 per cent. barium acetate solution. The precipitate of barium sulphate and fluoride is then subjected to the etching test.\*

6. **Calcium Chloride** gives a white, slimy precipitate, difficultly soluble in hydrochloric and nitric acids, but almost entirely insoluble

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\* Cf. Blarez, Chem. News, 91, 39; also Woodman and Talbot, J. Am. Chem. Soc., 27, p. 1437.

ble in acetic acid. On account of its slimy consistency, the precipitated calcium fluoride is extremely hard to filter; but by precipitating it in the presence of calcium carbonate a mixture is obtained which can be readily filtered. After igniting and treating with acetic acid, the precipitate is changed to soluble calcium acetate and insoluble calcium fluoride; it is now much denser and can be filtered readily.

7. **Ferric Chloride** produces in concentrated solutions of alkali fluorides a white, crystalline precipitate corresponding to the general formula  $[\text{FeF}_6]\text{X}_3$ . These salts, which are analogous to cryolite,  $[\text{AlF}_6]\text{Na}_3$ , are difficultly soluble in water, and their saturated, aqueous solutions do not give the iron reaction upon the addition of potassium sulphocyanate, except after the addition of acid. These complex fluorides also are incompletely decomposed by ammonia, basic fluorides being formed.

#### Methods for Getting Insoluble Fluorides into Solution.

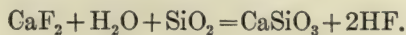
(a) Calcium fluoride alone cannot be completely decomposed by fusing with sodium carbonate. The aqueous solution of the melt always contains a considerable amount of sodium fluoride, but never the total amount of the fluorine. If, however, the fluoride is mixed with silica or a silicate, complete decomposition can be effected by fusing with sodium carbonate.

On treating the melt with water, sodium fluoride and sodium silicate go into solution, while the calcium is left behind on the carbonate, and can be dissolved by treatment with dilute hydrochloric acid.

(b) All fluorides are decomposed by heating with concentrated sulphuric acid, being changed to sulphates.

#### REACTIONS IN THE DRY WAY.

Most fluorides are unchanged by ignition. By heating them with silica in moist air, they are all more or less completely decomposed:

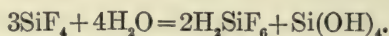




The acid fluorides give off hydrofluoric acid on ignition, whereby the glass tube in which they are heated becomes etched.

### HYDROFLUOSILICIC ACID, $\text{H}_2\text{SiF}_6$ .

As we have seen, this acid is formed by the action of silicon fluoride upon water:



If the silicic acid is filtered off, a strongly-acid solution is obtained containing hydrofluosilicic acid. By evaporating the solution, the acid is decomposed into silicon fluoride and hydrofluoric acid,



so that hydrofluosilicic acid itself is only known in aqueous solution, although its salts are very stable.

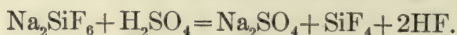
*Solubility.*—Most silicofluorides are soluble in water; the potassium and barium salts form exceptions, being difficultly soluble in water and insoluble in alcohol.

### REACTIONS IN THE WET WAY.

A solution of sodium silicofluoride should be used.

1. **Dilute Sulphuric Acid** causes only a very slight decomposition.

2. **Concentrated Sulphuric Acid** decomposes all silicofluorides, evolving silicon fluoride and hydrofluoric acid:



If the reaction is performed in a platinum crucible, the escaping gas will etch glass, and will cause a drop of water to become turbid.

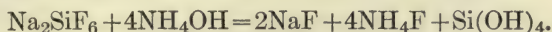
3. **Silver Nitrate** produces no precipitation.

4. **Barium Chloride** gives a crystalline precipitate (1 part of the salt dissolves at  $17^\circ\text{C}$ . in 3731 parts of water).

5. **Potassium Chloride** produces, from solutions which are not too dilute, a gelatinous precipitate of potassium silicofluoride, which is difficultly soluble in water (833 parts of water dissolve at  $17^\circ\text{C}$ .

one part of the salt) and much more insoluble in an excess of potassium chloride or in alcohol, but soluble in ammonium chloride.

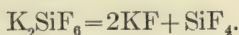
6. **Ammonia** decomposes all soluble silicofluorides, with separation of silicic acid:



7. **Potassium and Sodium Hydroxides** react in the same way as ammonia, but the silicic acid remains in solution as alkali silicate.

#### REACTIONS IN THE DRY WAY.

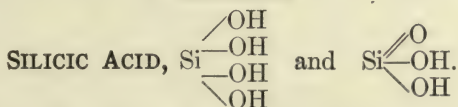
All silicofluorides are decomposed on being heated into fluoride of the metal and silicon fluoride:



The escaping gas renders a drop of water turbid, and the residue gives all the reactions of a fluoride.

### GROUP VII.

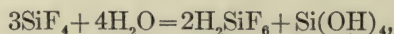
#### NON-VOLATILE ACIDS WHICH FORM SOLUBLE SALTS WITH THE ALKALIES.



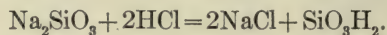
*Occurrence.*—The above acids, from which very stable salts are derived, are not known in the free state, as is the case with carbonic and sulphurous acids; although there are indeed amorphous, natural minerals consisting of hydrated silica with varying amounts of water: water opal with about 36 per cent. water, ordinary opal with from 3 to 13 per cent. water, and hyalite with about 3 per cent. water; but none of these substances represents a compound of constant composition.

The anhydride  $\text{SiO}_2$  occurs in rhombohedral crystals as quartz, whose prismatic faces are almost always striated horizontally; and as tridymite, also crystallizing in the hexagonal system. The amorphous silicic acid is often found mixed with the crystallized anhydride as flint, agate, chalcedony, jasper, etc. Silicic acid is, however, most frequently found in the form of its salts, the silicates.

*Preparation and Properties.*—Silicic acid can be very readily obtained pure by the hydrolysis of its fluoride.



or by the decomposition of alkali silicates (water-glass) with acids:



The silicic acid thus obtained forms an amorphous, gelatinous mass, appreciably soluble in water and acids, and readily soluble in even dilute solutions of caustic alkalies or alkaline carbonates. Thus freshly-precipitated silicic acid will be readily and completely dissolved by a short digestion with 5 per cent. (or even 1 per cent.) sodium carbonate solution on the water-bath. On being dried, silicic acid gradually loses water, and at a gentle red heat is changed into the form of its anhydride. According to the extent to which the dehydration has gone, the solubility of the silicic acid diminishes both in acids and in alkalies.

1. Air-dried silicic acid, with 16.65 per cent. of water, corresponding to the formula  $3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , is perceptibly soluble in acids, and completely dissolved by digestion for  $\frac{1}{4}$  to  $\frac{1}{2}$  an hour with 1 per cent. soda solution on the water-bath.

2. Silicic acid dried at  $100^\circ$  with 13.60 per cent. of water, corresponding to the formula  $2\text{SiO}_2 \cdot \text{H}_2\text{O}$ , is practically insoluble in acids, but can be dissolved by digesting for  $\frac{1}{4}$  hour with 1 per cent. sodium carbonate solution upon the water-bath, or more readily by boiling.

3. Silicic acid dried at  $200^\circ$ , with 5.66 per cent. of water, corresponding to the formula  $5\text{SiO}_2 \cdot \text{H}_2\text{O}$ , and the acid dried at  $300^\circ$ , with 3.40 per cent. of water, corresponding to the formula  $9\text{SiO}_2 \cdot \text{H}_2\text{O}$ , dissolve slowly by digestion with 1 per cent. sodium carbonate solution on the water-bath.

4. The anhydride obtained by gentle ignition to a faint-red heat is only partly dissolved by 1 per cent. or by 5 per cent. sodium carbonate after half an hour's digestion on the water-bath; but is dissolved after boiling for two hours with the sodium carbonate solution.

5. The strongly-ignited anhydride is only soluble in 5 per cent. boiling sodium carbonate solution after repeated boiling for a long

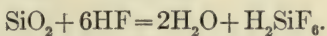


time, but is readily dissolved by boiling with concentrated caustic soda or potash.

6. The native anhydride, quartz, after being powdered in an agate mortar, is practically insoluble in 5 per cent. sodium carbonate solution, and extremely difficultly soluble in boiling caustic alkali. If it is in the form of an extremely fine powder, it can be dissolved by boiling with 5 per cent. sodium carbonate solution (Lunge and Millberg).

It follows from the above that the solubility of silicic acid (and of its anhydride) in alkali carbonates depends largely upon the fineness of the material.

Silicic acid, as well as its anhydride, is soluble in aqueous hydrofluoric acid, forming hydrofluosilicic acid:



By evaporating this solution hydrofluoric acid is evolved; and silicon fluoride, with small amounts of silicic acid, is left behind. In order, then, to completely volatilize silicic acid by means of hydrofluoric acid, the hydrolytic action of water must be prevented, which is effected by the addition of a little concentrated sulphuric acid. The process is as follows:

A little water, not more than  $\frac{1}{2}$  c.c. of concentrated sulphuric acid, and then the hydrofluoric acid, are added to the silica, and the mixture evaporated on the water-bath until the mass no longer smells of hydrofluoric acid, when the sulphuric acid is driven off by heating the crucible in an inclined position over a small flame. If considerable silicic acid is present, the operation must be repeated two, or perhaps three, times.

The salts of silicic acid, the silicates, are exceedingly numerous, and are usually very stable. Many of them are so stable that they are not attacked by concentrated acids, while others are easily decomposed thereby.

The different silicates are classified according to their solubility into

A. Water-soluble silicates.

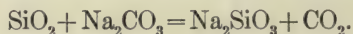
B. Water-insoluble silicates, which are again divided into

(a) Silicates decomposable by acids;

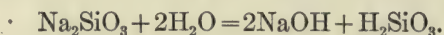
(b) Silicates undecomposable by acids.

**A. Water-soluble Silicates.**

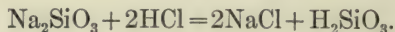
The silicates which are soluble in water, or "water-glasses," are obtained by fusing silica or a silicate with caustic alkali or alkali carbonate:



1. **Behavior Toward Acids.**—The aqueous solutions of an alkali silicate react strongly alkaline, showing that the salt is hydrolyzed to a marked degree:



The silicic acid set free by the hydrolysis is present as hydrosol in the solution. By the addition of acid the alkali hydroxide is converted into salt and a part of the silicic acid is coagulated, provided the solution is not too dilute.

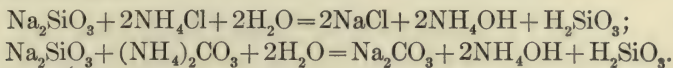


The precipitation is by no means quantitative; a considerable quantity of silicic acid remains in solution and, in fact, under some conditions all of it may remain dissolved in the dilute acid. If, namely, a ten per cent water glass solution is poured quickly into hydrochloric acid of specific gravity 1.1 to 1.3, there is no precipitation. After standing some time, however, the entire contents of the beaker are changed to a jelly. From 1 per cent solutions treated similarly with acid, no precipitate appears even after standing a year.

The silicic acid which is precipitated upon the addition of acid is, therefore, considerably soluble in dilute acids. In order to completely separate the silicic acid from a solution of water-glass, the hydrated acid must be changed into the less hydrated acid,  $2\text{SiO}_2 \cdot \text{H}_2\text{O}$ , by heating at  $100^\circ \text{C}$ . (cf. page 402). For this purpose the water-glass solution is acidified with hydrochloric acid (or nitric or sulphuric acid) and evaporated on the water-bath to complete dryness (the mass must no longer smell of acid). The dry residue

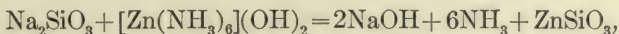
is treated with water to which a little acid has been added, and after filtration very little silicic acid remains dissolved.\*

**2. Behavior Toward Ammonium Salts.**—If a solution of water-glass is treated with an ammonium salt, the silicic acid will, for the most part, be precipitated as hydroxide; the precipitation is not quite quantitative, but more complete than is obtained by the addition of cold dilute acid:



The precipitation by means of ammonium carbonate is less complete than in the case of an ammonium salt of a stronger acid, on account of the formation of sodium carbonate, which exerts a solvent action upon the precipitate. We are, nevertheless, often compelled to use this reagent, as, for example, when it is desired to test a silicate for chlorine or fluorine (cf. page 398).

Silicic acid is more completely precipitated by zinc ammonium hydroxide than by ammonium carbonate,



because the zinc silicate formed by the reaction is much more difficultly soluble in dilute alkaline solution than is the free silicic acid.

The separation of silicic acid from a solution of water-glass by means of ammonium carbonate may be illustrated by a common case. Many rocks (particularly the zircon-syenite of Norway and Greenland, many granites and basalts) contain small amounts of sodalite,  $\text{NaCl} \cdot 3\text{NaAlSiO}_4$ , a chloride silicate of the leucite group. In order to detect the chlorine in such a rock, the following process may be used: The finely-powdered silicate is fused with six times as much sodium carbonate in a platinum crucible, and the product of the fusion is treated with cold water and filtered. The filtrate contains all of the chlorine as sodium chloride in the presence of sodium silicate. The solution is treated with ammonium carbonate, warmed gently, allowed to stand twelve hours, and the

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\* The small amount of silica remaining in solution can be removed almost entirely by a second evaporation of the filtrate. Cf. Hillebrand, *J. Am. Chem. Soc.*, 1902, p. 362.



precipitated silicic acid filtered off. In order to separate the rest of the silicic acid, a little zinc ammonium hydroxide \* is added and the solution boiled until it no longer smells of ammonia. The precipitated zinc silicate and zinc oxide are filtered off, the solution acidified with nitric acid and tested with silver nitrate for chlorine.

## B. Silicates Insoluble in Water.

### (a) *Decomposable by Acids.*

A large number of native silicates are decomposed by evaporation with hydrochloric acid, the silica being deposited sometimes in the form of a jelly and sometimes in the form of a powdery mass. All zeolites, and a number of artificial silicates (such as Portland and Roman cements) belong to this class of silicates.

In order to remove all of the silicic acid from these silicates, the finely-powdered mineral is treated with dilute hydrochloric acid, evaporated on the water-bath to dryness, the mass moistened with concentrated hydrochloric acid,† allowed to stand for 20 minutes, hot water added, and the solution boiled and filtered. The silicic acid is left on the filter, and the filtrate contains the metals as chlorides.‡

The purity of the residual silicic acid must always be tested. For this purpose the well-washed precipitate is placed, together with the filter-paper, in a clean platinum crucible, held in an inclined position on a triangle, and the filter-paper carefully burnt. The residue is treated with about 2 c.c. of water, a drop of concentrated sulphuric acid, and about 3–5 c.c. of pure hydrofluoric acid, and evaporated as far as possible on the water-bath. The excess of sulphuric acid is then removed by cautious heating over the free flame. If the silicic acid were pure, nothing should remain after the evaporation of the sulphuric acid. Almost always a small residue of aluminium and ferric oxides remains, which in most cases can be

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\* Prepared by dissolving pure zinc in nitric acid, treating the solution with potassium hydroxide solution until it is neutral, and dissolving the filtered and washed zinc hydroxide in ammonia.

† The moistening with concentrated hydrochloric acid serves to convert any oxides or basic salts of iron, aluminium, magnesium, etc., into soluble chlorides.

‡ Cf. page 405.—Foot note.

neglected. If considerable residue is left, it should always be tested for titanitic acid and barium sulphate.

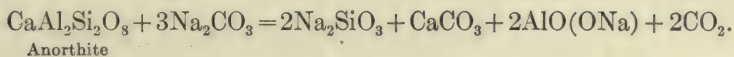
(β) *Silicates Undecomposable by Acids.*

Most silicates, the feldspars, micas, artificial glasses, porcelain, etc., belong to this class. In order to remove the silicic acid from such substances, they must be

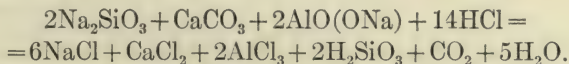
1. Fused with an alkali carbonate,
2. Fused with lead oxide or boron trioxide, or
3. Heated with sulphuric and hydrofluoric acids.

1. *Fusion with an Alkali Carbonate.*—This method is commonly used when it is desired to detect the presence of silicic acid and of the bases with the exception of the alkalies.

The finely-powdered substance is mixed with 4–6 times as much calcined sodium carbonate (or a mixture of equal parts of sodium and potassium carbonates, which melts lower than sodium carbonate alone), placed in a platinum crucible and heated carefully at first to avoid spattering from too violent evolution of carbon dioxide. The temperature is gradually increased until the full heat of the burner is reached, and the fusion continued until the molten mass is quiet, when it is heated for about a quarter of an hour over the blast lamp. The crucible is then cooled quickly by dipping it while still glowing into cold distilled water, whereby the fused mass can usually be removed from the crucible without difficulty.\* The product of the fusion is treated as previously described under (α), being now converted into either sodium silicate or a silicate decomposable by acid.



By evaporation with hydrochloric acid, the following reaction takes place:



During the evaporation to dryness salts like aluminium chloride, (ferric chloride, etc.) are subject to hydrolysis and are converted

\* For another excellent method for removing the melt from the crucible see Talbot's Quantitative Chemical Analysis.

to some extent into oxide or basic salt, insoluble in water. Therefore, in order to separate the silicic acid from the salts, it is first necessary to convert such oxides or basic salts back into chlorides. This is accomplished by moistening the dry residue with concentrated hydrochloric acid. After allowing the acid to act for ten or fifteen minutes at the ordinary temperature, hot water is added and the silicic acid filtered upon an ashless filter.

To identify the silicic acid, the well-washed precipitate together with the filter is placed in a weighed platinum crucible, dried carefully by a low flame placed in front of the crucible, and then ignited at as low a temperature as possible, with the flame now at the base of the crucible, until the carbon of the filter is all consumed. The crucible and its contents are then weighed and the ignited silica volatilized by treatment with sulphuric and hydrofluoric acids as described in Vol. II. A difference in the weights before and after the treatment with these acids shows not only the presence of silica, but also the quantity of it. This quantitative method is to be recommended for the recognition of small quantities of silicic acid.

To identify the silicic acid qualitatively, Daniel's tetrafluoride test is satisfactory.\*

The well-washed precipitate is ignited, as described above, in a platinum crucible, then triturated in a mortar with three times as much potassium-sodium carbonate, and the mixture is then fused in the crucible. After cooling the melt, it is softened by heating with a little water and treated with dilute sulphuric acid to decompose the excess of carbonate as well as the salt of silicic acid formed during the fusion. The mixture is heated in the crucible, by placing the latter upon a piece of asbestos board, and evaporated nearly to dryness, or until a thick jelly of silicic acid remains. After cooling, there is added three times as much fluorspar as there was original precipitate, a little magnesite and enough concentrated sulphuric acid to make a thin paste. After mixing the contents of the crucible with the aid of a stout platinum wire, a drop of water is placed on the inside of the crucible cover, which is partly painted with asphaltum, the cover is placed on the crucible and the contents of the latter heated

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\* *Z. anorg. Chem.*, 38, 299 (1904).



gently. From time to time, the cover is raised to see whether the water has become turbid. If frequently happens that the water becomes turbid, and then, provided a large excess of hydrofluoric acid is present, the turbidity disappears. For this reason the cover must be inspected frequently in order not to miss any temporary turbidity.

The tetrafluoride test for silicic acid is very sensitive if the reaction is carried out in a very small platinum crucible. If such a crucible is not at hand, with a capacity of say 0.5 to 1 c.c., it is better to test by the quantitative method when less than 0.01 gm. of silicic acid is present.

2. *Fusion with Lead Oxide or Boron Trioxide.*—These methods are very rarely used in qualitative analysis, so that it will not be necessary to describe them here. They play an important part in quantitative analysis, and will be described, therefore, in the second volume of this book.

3. *Decomposition by Hydrofluoric Acid.*—This method is used principally when a silicate is to be examined for alkalies, titanitic acid or barium. The finely-powdered silicate is placed in a platinum dish, about 2 c.c. of pure sulphuric acid (1 vol. concentrated acid and 2 vols. of water) and about 5 c.c. of freshly-distilled hydrofluoric acid are added, and the mixture evaporated on the water-bath, stirring the mass from time to time with a thick platinum wire until it no longer smells of hydrofluoric acid. 5 c.c. more of hydrofluoric acid are added and again evaporated, whereupon the dish is heated very carefully over the free flame under a good hood, until the greater part of the sulphuric acid is expelled.\* After cooling, the mass is treated with water, when usually everything will by degrees go into solution. If a residue remains, it is tested for barium sulphate and titanitic acid. The solution can be used for the alkali tests, or for the tests for the other metals if it is desired.

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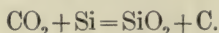
\* The mass should not be ignited strongly, for a part of the sulphate may then be changed to an oxide insoluble in water. The sulphates of iron and aluminium, for example, are decomposed on ignition.

## REACTIONS IN THE DRY WAY.

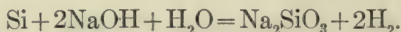
If silicic acid or a silicate is heated in the salt of phosphorus bead, the metallic oxide will dissolve, while the silicic acid itself will be left as a white gelatinous mass, suspended in the bead (skeleton bead). This reaction is, however, not infallible, for certain silicates of the zeolite group dissolve in the bead without the formation of the skeleton.

**SILICON, Si. At. Wt. 28.3,**

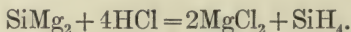
Silicon exists in two modifications, one of which is crystalline, while the other is amorphous. Amorphous silicon is a dark-brown powder, which can be oxidized by heating in the air while the crystalline modification remains unchanged on ignition in pure air or in oxygen, but if the air contains carbon dioxide, it is oxidized to silicon dioxide with deposition of carbon:



Crystallized silicon is not attacked by any acid, but is readily dissolved by boiling with concentrated caustic alkali with evolution of hydrogen:



Silicon unites with many metals, forming silicides. The silicides of the light metals, magnesium, calcium, etc., are decomposed by dilute hydrochloric acid with the formation of spontaneously-combustible silicon hydride \*:



In order to detect the presence of silicon in such a compound it is treated with nitric acid, which oxidizes the greater part of the silicon to silicic acid.

If it is a question of detecting the presence of silicon in the different kinds of irons (steel, cast iron, etc.), a large amount of material should be taken, for the amount of iron silicide present is usually very small. Five or ten grams of the material to be tested (best in

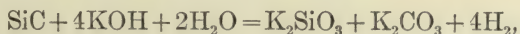
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\* The hydride of silicon is not spontaneously combustible when pure, only when it is contaminated with hydrogen, as is invariably the case.

the form of borings) are placed in a large beaker and treated with 60 c.c. of nitric acid (sp. gr. 1.2). A violent reaction at once takes place with evolution of brown nitrous fumes. As soon as this action lessens, it is heated to boiling, and the heating continued until no more brown fumes are given off, when it is poured into a 200-c.c. evaporating-dish of Berlin porcelain and evaporated as far as possible upon the water-bath. It is then heated, with constant stirring, over a free flame until completely dry. The dry mass is ignited until the nitrate is completely changed to oxide, when no more brown fumes will be evolved. After cooling, the mass is dissolved in about 50 c.c. of concentrated hydrochloric acid, heated with constant stirring almost to boiling, evaporated almost to dryness, taken up in water, filtered, and the residue tested for silicic acid, by seeing whether it is volatile with sulphuric and hydrofluoric acids.

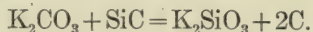
In the case of cast iron, the silicic acid obtained is usually considerably contaminated with graphite, which can be removed by long ignition in a platinum crucible before treating with hydrofluoric and sulphuric acids.

Other silicides, such as carborundum,  $\text{SiC}$ , are not decomposed by nitric acid; they can be fused with caustic alkali in a silver crucible,

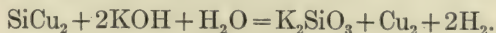


and on acidifying the melt, the silicic acid separates out.

Carborundum in the form of a fine powder is also easily decomposed by fusing with potassium carbonate. On removing the cover of the platinum crucible the blue flame of burning carbon monoxide is apparent,



The method of fusing silicides with caustic alkali is often used for getting metallic silicides into solution. Many copper silicon alloys are scarcely attacked by even aqua regia. If, however, they are fused with caustic alkali in a silver crucible, potassium silicate, metallic copper, and hydrogen are formed:



By treating the melt with water, the soluble potassium silicate may be separated from the copper.



## PART II.

### COURSE OF ANALYSIS.

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THE purpose of a qualitative analysis is not simply to find out what elements are contained in a given substance, but it should also give a good idea of the relative amounts that are present. Manganese chloride, for example, is made from pyrolusite, and almost always contains traces of calcium, magnesium, nickel, cobalt, and iron. If the analyst should report that "the analyzed substance consists of chlorides of calcium, magnesium, nickel, cobalt, iron, and manganese," it is evident that one would get but a poor idea of the nature of the substance. The report should read: "The substance examined was manganese chloride, and contained traces of calcium, magnesium, etc., as impurities."

In order to be able to estimate the relative amounts of the different components of a substance, it is necessary to start with a known amount (usually  $\frac{1}{2}$ –1 gm.) and compare the size of the precipitates produced. It will be impossible for the beginner to estimate the amount of a precipitate obtained, if he has studied the reactions of the elements with unknown amounts of the different substances. If he has learned to work with a known amount of material, he will soon be able to judge from the size of a precipitate the amount of element to which it corresponds.

Every analysis should be divided into three parts:

- I. *The preliminary examination.*
- II. *The examination for the metals (cations).*
- III. *The examination for the negative elements (anions).*

The substance analyzed can be

- A. *Solid and non-metallic.*
- B. *A metal or an alloy.*
- C. *A solution (liquid).*
- D. *A gas.*

The whole amount of the substance at hand should never be used for the first analysis, but a portion should always be reserved for unforeseen accidents. The portion taken for analysis should be divided into two parts after the preliminary examination, the first part being used for the tests for the electro-positive and the other part for the tests for the electro-negative elements.

Before beginning an analysis, the substance should be carefully examined with the naked eye and with the microscope, and the results noted. Oftentimes the smell, color, and crystalline form suffice to give important clues as to the nature of the substance.

## A. THE SUBSTANCE IS SOLID AND NON-METALLIC.

### I. PRELIMINARY EXAMINATION.

This should never be omitted, for it often shows how the subsequent analysis may be considerably shortened, and in some cases makes the further examination unnecessary. It consists only of making the following few simple tests:

1. **Heating in the Closed Tube.**—By a closed tube is understood a small test-tube, or a glass tube sealed at one end. A small amount of the substance to be tested is placed in the tube so that none of it remains adhering to the sides. The tube is held in a nearly horizontal position and cautiously heated in the flame, while the observer notes carefully whether any changes take place.

#### The Substance is Volatile.

(a) The substance sublimes completely without any deposition of water; it contains no non-volatile substance.

The sublimate is white. The halogen compounds with ammonia, mercurous chloride and bromide, mercuric aminochloride, arsenic trioxide and arsenic pentoxide \* may be present.

The sublimate is colored—

Gray: all oxygen compounds of mercury, cyanide of mercury, † free iodine, and arsenic.

Yellow: arsenic sulphide, sulphur, mercuric iodide. ‡

Grayish black: mercuric sulphide.

(b) The substance is completely volatile, with separation of

\* Arsenic pentoxide melts before being changed into the trioxide.

† Mercuric cyanide leaves a brown mass, paracyanide, which only disappears after long-continued heating.

‡ Mercuric iodide becomes red immediately on being rubbed with a glass rod.

water and gaseous products: most ammonium compounds (with the exception of those of the halogens) and free oxalic acid.\*

### The Substance is Only Partly Volatile.

In this case gases and vapors may be evolved:

Oxygen from peroxides, nitrates, chlorates, iodates, etc.

Carbon dioxide from carbonates and organic substances; in the latter case it is usually accompanied with the separation of carbon and evolution of empyreumatic, combustible vapors.

Chlorine from chlorides of platinum, gold, copper, iron, etc.

Iodine from iodides, in the presence of oxidizing substances.

Sulphur from many sulphides and thiosulphates.

Arsenic from arsenites † and arseniates, in the presence of carbon or organic substances.

Water from substances containing water of crystallization, from acid salts, organic substances, or from the phosphate, borate, chromate, vanadate, and tungstate of ammonium.

The water given off condenses in the cooler part of the tube and should be tested with litmus-paper. If it reacts alkaline, it comes from ammonium compounds; if acid, it results from easily decomposable salts of the stronger acids.

Many fluorides when heated with water give off hydrofluoric acid, which etches the glass.

If a sublimate is formed, the following experiment is made:

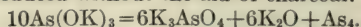
**2. A Portion is Mixed with Three Times as Much Calcined Sodium Carbonate and Heated in the Closed Tube.**—If ammonium salts are present, the smell of ammonia can be detected. Mercury compounds give a deposit of gray metal (cf. page 182); arsenic and its oxygen compounds also usually yield the gray metal, ‡ (but no globules) accompanied by a garlic odor.

**3. The Substance is Tested in the Bead.**—A bead of borax, or salt of phosphorus, is produced in the loop of a very thin platinum wire (as described on page 33), introduced with a little of the substance into the oxidizing flame, and the color of the bead observed both when it is hot and when it is cold, after which it is

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\* By very cautious heating, oxalic acid may be sublimed; it usually decomposes, however, into water, carbon monoxide, and carbon dioxide.

† Arsenites are reduced without the aid of charcoal:



‡ The oxygen compounds of arsenic do not give the metal when heated with pure soda. Commercial soda, however, is usually contaminated with paper threads, which cause the reduction.



heated in the reducing flame. Borax is usually used for this experiment, except when it is desired to test for silicic or titanlic acids, or when the substance is white, in which case salt of phosphorus is used. Only colored oxides are capable of coloring the borax bead.\*

The following substances impart a characteristic color to the bead: iron, manganese, nickel, cobalt, chromium, uranium, copper (didymium, cerium, vanadium, titanium, and tungsten).

As the coloration varies with the temperature and with the amount of substance used, the results to be expected, with the necessary conditions, are summarized in the following table. The following abbreviations will be used: h=hot; c=cold; h—c=hot and cold; s.s.=slightly saturated; sat.=saturated.

Color of the Bead.	WITH BORAX.		WITH SALT OF PHOSPHORUS.	
	In the Oxidizing Flame.	In the Reducing Flame.	In the Oxidizing Flame.	In the Reducing Flame.
Colorless	SiO <sub>2</sub> (without skeleton), alkaline earths, Hg, Pb, Bi, Sb, Cd, Zn, Sn, Ti	SiO <sub>2</sub> (without skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)	SiO <sub>2</sub> (usually with skeleton), alkaline earths and earths (sat. =turbid)	SiO <sub>2</sub> (usually with skeleton), alkaline earths and earths, Mn, Di, Ce, Cu (s.s.)
	W, Mo, Fe (s.s.—c)		W, Ti	
Gray		Ag, Pb, Bi, Sb, Cd, Zn, Ni		Ag, Pd, Bi, Sb, Cd, Zn, Ni
Yellow (or brown)	Fe (s.s.—h), Ag (h), Ce (h), U (h), V (h—sat.), Ni (c) (brown)	Ti (h), W (h), V (h), Mo (h)	Fe (s.s.—h), Ag (h), Fe (sat.—c), Ce (h), V (h), U (h), Ni (c) (brown)	Fe (h), Ti (h)
Green	Cr (c), Cu (h)	Fe (h—c), Ur, Cr. V (h)	Cr (c), Cu (h), Mo (h), U (c—sat.)	Cr (c), U (c), V (c), Mo (c)
Blue	Co (h—c), Cu (c)	Co (h—c)	Co (h—c), Cu (c)	Co (h—c), W (c)
Violet	Mn (h—c), Di (h—c), and Ni (with cobalt)		Mn (h—c), Di (h—c)	Ti (c)
Red	Fe (h—sat.), Ce (h)	Cu (sat.), opaque; when very slightly saturated and with a trace of Sn, ruby red and transparent.	Fe (h—sat.) Ce (h)	Cu as in the borax bead; Ti and W in the presence of iron = blood red

\* Some are reduced to metal, so that the bead appears gray in the reducing flame (see table). CuSO<sub>4</sub> is white when anhydrous, but becomes blue immediately on the addition of water.

4. A Small Sample is Heated by Itself upon Charcoal before the Blowpipe, and if deflagration takes place a nitrate, nitrite, chlorate, iodate, etc., may be present.

5. The Substance is Heated with Soda upon Charcoal before the Blowpipe.—As much of the substance as can be taken up on the end of a knife-blade is mixed with twice as much sodium carbonate (as described on page 38), placed in the cavity of a piece of charcoal and heated in the reducing flame of the blowpipe.

There is obtained

- |   |   |   |
|---|---|---|
|   | { | As malleable button: Au, Ag, Sn, Cu, which can be pressed flat in an agate mortar.  |
| (a) Metal without incrustation.                   | { | As gray metallic particles: Pt, Fe, Ni, and Co. Pt may be pressed flat in an agate mortar; Fe, Ni, and Co are magnetic and are attracted by a magnet (cf. page 35). |
|   | { | As a brittle metallic button: Sb (white incrustation), Bi (yellow incrustation). The button may be reduced to a powder by grinding in an agate mortar.              |
| (b) Metal with incrustation....                   | { | As a malleable button: Pb (yellow incrustation).  |
|   | { | White, yellow when hot: Zn.   |
| (c) Incrustation without metal.                   | { | Brown: Cd.  |
|   | { | White: As (garlic odor).  |
| (d) White, infusible, strongly luminous mass..... | { | Ca, Sr, Mg, Al, and rare earths.  |

(e) Sulphur compounds are reduced to sulphides. If the melt is placed on a bright silver coin and moistened with water, the silver is blackened (Hepar reaction).

6. The Substance is Tested to See Whether it Imparts Any Color to the Non-luminous Flame.—A small sample is introduced by means of a platinum wire into the base of the flame (cf. page 33), and then into the fusing zone. It is afterwards moistened with dilute hydrochloric acid and the experiment repeated. The following indications may be obtained:

**Sodium** gives a yellow mono-chromatic flame; a piece of sealing-wax or a crystal of potassium dichromate appears yellow when illuminated by this flame.

**Potassium** (caesium and rubidium) gives a violet flame which is completely obliterated by the sodium flame. If the flame is observed through cobalt glass, the sodium flame disappears and the potassium flame appears pink.

**Lithium** gives a carmine-red flame (or a red line in the spectro-scope).

**Strontium** also gives a carmine-red flame (which the spectro-scope shows to consist of several lines in the orange, and a bright line in the blue).

**Calcium** gives a brick-red flame (in the spectro-scope an orange and a green line are seen, both about an equal distance away from the sodium line).

**Barium** gives a greenish-yellow flame.

In the case of barium sulphate the green flame is either only indistinctly visible or not at all. In order to detect barium in this case, a small portion of the substance is heated in the upper reducing flame; after cooling it is moistened with hydrochloric acid (odor of hydrogen sulphide) and again heated, when the barium flame can be easily seen.

**Thallium** gives an emerald-green flame.

Another portion of the substance should then be tested for boric acid, by treating with concentrated sulphuric acid and bringing near the flame. A green color indicates the presence of boric acid, but if copper is present this test cannot be relied on.\*

**Lead, Arsenic, Antimony** color the flame light blue, and **copper** compounds color the flame either green or blue.

### Preliminary Examination for the Electro-negative Elements (Anions).

1. **Dilute Sulphuric Acid** (double normal).—About a gram of the substance is treated in a small test-tube with dilute sulphuric acid, and one notes whether a reaction takes place in the cold or not (evolution of a gas).

The following gases can be recognized:

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\* By heating the solid substance with potassium ethyl sulphate in a test-tube, boric acid is converted into  $B(OC_2H_5)_3$ , which burns with a green flame. Copper chloride does not interfere with this test. V. Castellina, Chem. Zentrabl., 1905, I, p. 1619.



HCN from cyanides (odor\*);

H<sub>2</sub>S from soluble sulphides (odor, and blackening of lead acetate paper);

NO<sub>2</sub> from nitrites (brown fumes);

SO<sub>2</sub> without separation of sulphur from sulphites (odor of burning sulphur);

SO<sub>2</sub> accompanied by separation of sulphur from thiosulphates. the deposited sulphur is yellow, particularly after warming;

CO<sub>2</sub> from carbonates or cyanates (barium hydroxide solution is rendered turbid).

By boiling with dilute sulphuric acid, soluble ferro- and ferricyanides are decomposed and evolve hydrocyanic acid; acetates, set free acetic acid; hypochlorites evolve chlorine (which also takes place in the cold); while the peroxides of the alkalies † and alkaline earths are decomposed with evolution of oxygen.

**2. Concentrated Sulphuric Acid.**—If the substance does not react with dilute sulphuric acid, a new portion is treated with 3 or 4 c.c. of concentrated sulphuric acid and heated. If the substance reacted with dilute sulphuric acid, it will react violently with concentrated sulphuric acid and the gas will come off so quickly that it will carry small particles of the sulphuric acid with it, which makes the gas appear to have a penetrating odor and may lead to a mistaken conclusion, especially as it will also cause barium hydroxide solution to become turbid.

In such a case, dilute sulphuric acid is added drop by drop to a new portion of the substance until no further action takes place when five c.c. of concentrated sulphuric acid are added and the mixture warmed.

Gases and vapors may be evolved, which are

(a) *Colorless.*

HCl from chlorides, fuming in the air, with a penetrating odor. The fumes do not cause a turbidity with water.‡

SiF<sub>4</sub>§ from fluorides, fuming in the air, with a penetrating

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\* Mercuric cyanide does not liberate HCN in this test.

† Alkali peroxides evolve oxygen when treated with water. Cf. p. 52.

‡ AgCl and HgCl<sub>2</sub> only slowly evolve HCl; similar with Hg<sub>2</sub>Cl<sub>2</sub>, and in this case SO<sub>2</sub> is also set free. Cf. p. 281.

§ SiF<sub>4</sub> is formed on account of the experiment being performed in glass. In platinum, HF would be evolved in the absence of silica, which does not render water turbid.

odor, and causing a turbidity on coming in contact with water.

$\text{SO}_2$  *without* separation of sulphur. If there was no evolution of sulphur dioxide on treatment of the substance with dilute sulphuric acid, the sulphur dioxide which now escapes must come from the sulphuric acid itself; a metal, sulphur, a sulphide, carbon, or non-volatile organic matter, such as tartaric acid, citric acid, sugar, starch, etc., must be present. If non-volatile organic matter is present, carbonization will take place on warming.

$\text{SO}_2$  *with* separation of sulphur indicates the presence of a sulphocyanate, in case there was no action with dilute sulphuric acid.

CO from oxalates and other organic substances, and cyanates. It is an odorless gas, which does not fume in the air and burns with a blue flame.

(b) *Colored.*

Cl, a yellow gas with a suffocating odor, turns iodo-starch paper blue, and indicates the presence of both a chloride and an oxidizing substance.

$\text{ClO}_2$ , a yellow gas, very similar to chlorine, but which explodes violently on being heated, indicates a chlorate. If the substance deflagrates on being heated on charcoal, only a small portion of the substance should be used for this test; but if no explosion takes place on warming, more of the substance should be added.

HBr from bromides has a penetrating odor, fumes in the air, and is always colored yellowish brown by the presence of small amounts of bromine. The sulphuric acid is at first colored brown in the case of a colorless bromide, but becomes colorless on being boiled.

$\text{CrO}_2\text{Cl}_2$ , brown (similar to bromine), results from the presence of a chloride and chromic acid.

$\text{I}_2$ , violet. In the case of a colorless iodide, the sulphuric acid is at first colored brown by small amounts of iodide, or gray, solid iodine is deposited if considerable iodide is present, which volatilizes on warming, forming violet vapors. If considerable iodide is used for this test, the sulphuric acid is reduced to  $\text{SO}_2$ , or even  $\text{H}_2\text{S}$  (cf. page 294).

$\text{Mn}_2\text{O}_7$ , violet, is formed from permanganic acid, and is decomposed with scintillation, often exploding on being warmed.

$\text{NO}_2$ , brown, with a penetrating odor, comes from nitrates. After the preceding tests have been made, the next step is the

### Solution of the Substance.

As solvents the following are used:

1. Water;
2. Hydrochloric acid;
3. Nitric acid;
4. Aqua regia.

In the majority of cases the first three solvents suffice, aqua regia being only necessary in a comparatively few cases, as will be seen from the following table:

### SOLUBILITY TABLE.

#### SUBSTANCES SOLUBLE IN WATER.

Of Group I (page 276) the following are soluble:

1. **Chlorides.**—All except  $\text{AgCl}$ ,  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PtCl}_2$ ,  $\text{AuCl}$ ,  $\text{BiOCl}$ ,  $\text{SbOCl}$ ,  $\text{Mg}_2\text{OCl}_2$ .  $\text{PbCl}_2$  and  $\text{TlCl}$  are difficultly soluble.

2. **Bromides.**—The same as the chlorides.

3. **Iodides.**—All except  $\text{AgI}$ ,  $\text{Hg}_2\text{I}_2$ ,  $\text{HgI}_2$ ,  $\text{Cu}_2\text{I}_2$ ,  $\text{PdI}_2$ ,  $\text{TlI}$ ;  $\text{PbI}_2$  is very difficultly soluble.

4. **Cyanides.**—Only the cyanides of the alkalis, alkaline earths, and mercury.

5. **Ferrocyanides.**—Only those of the alkalis and alkaline earths.

6. **Ferricyanides.**—Same as the ferrocyanides.

7. **Cobalticyanides.**—Only those of the alkalis, alkaline earths, and the ferric, mercuric, and lead salts.

8. **Sulphocyanates.**—Those of the alkalis, alkaline earths, iron, cupric copper, and mercuric mercury.

9. **Hypochlorites.**—All.

Of Group II (page 276) the following are soluble:

10. **Nitrites.**—All. Silver nitrite is difficultly soluble.

11. **Acetates.**—Silver and mercurous acetates and certain basic acetates are difficultly soluble.

12. **Cyanates.**—Those of the alkalis, alkaline earths, and most of the remaining ones. Silver and lead cyanates are insoluble.



13. **Sulphides.**—Only those of the alkalies and alkaline earths. CaS is difficultly soluble.

14. **Hypophosphites.**—All.

Of Group III (page 276) the following are soluble:

15. **Sulphites.**—Those of the alkalies, and the bisulphites of the alkaline earths.

16. **Carbonates.**—Those of the alkalies, and the bicarbonates of Ca, Sr, Ba, Mg, Fe, Mn.

17. **Oxalates.**—Those of the alkalies; the remainder are difficultly soluble or insoluble. Most oxalates, however, with the exception of Ba, Ca, and Sr oxalates, form soluble complex salts with alkali oxalates.

18. **Iodates.**—Only those of the alkalies.

19. **Borates.**—Those of the alkalies. The remaining borates are all difficultly soluble in water, but soluble in ammonium chloride as a rule.

20. **Molybdates.**—Only those of the alkalies.

21. **Selenites.**—Those of the alkalies are readily soluble, the remaining ones are difficultly soluble.

22. **Selenates.**—All except the barium and lead salts.

23. **Tellurites.**—Only those of the alkalies.

24. **Tellurates.**—Only those of the alkalies.

25. **Tartrates.**—The normal tartrates of the alkalies, and lithium and sodium bitartrates. The remaining tartrates are insoluble in water, but are usually soluble in an excess of alkali tartrate solution, forming complex salts.

26. **Citrates.**—Only those of the alkalies are readily soluble in water. The insoluble citrates usually dissolve in an excess of alkali citrate solution.

27. **Pyrophosphates.**—Only those of the alkalies.

28. **Metaphosphates.**—Only those of the alkalies.

Of Group IV (page 276) the following are soluble:

29. **Phosphates.**—Only those of the alkalies.

30. **Arsenites.**—Only those of the alkalies.

31. **Arseniates.**—Only those of the alkalies.

32. **Thiosulphates.**—Almost all are soluble, though the silver and barium salts are difficultly soluble.

33. **Chromates.**—Those of the alkalies, Ca, Sr, Mg, Zn, Mn, Fe,

and Cu are soluble, the others are difficultly soluble or insoluble.

**34. Vanadates.**—The orthovanadates are unstable; the pyro-, meta-, and polyvanadates are soluble in water, as a rule. The lead and mercurous salts are insoluble, also the vanadates of the iron group.

**35. Periodates.**—All more or less soluble in water, except silver periodate, which is insoluble.

Of Group V (page 276), the following are soluble:

**36. Nitrates.**—All except a few basic salts.

**37. Chlorates.**—All.

**38. Perchlorates.**—All.

**39. Manganates and Permanganates.**—All.

Of Group VII (page 276), the following are soluble:

**40. Sulphates.**—All except the Ca, Ba, Sr, and Pb salts, and a few basic sulphates.

**41. Fluorides.**—Those of the alkalies, silver, and mercury; the remaining fluorides are difficultly soluble or insoluble in water.

Of Group VII (page 277), the following are soluble:

**42. Silicates.**—Only those of the alkalies.

**43. Tungstates.**—Only those of the alkalies.

*Of the salts insoluble in water, all dissolve in acid (hydrochloric or nitric) except AgCl, AgBr, AgI, AgCN, AuCl, PtCl<sub>2</sub>, BaSO<sub>4</sub>, SrSO<sub>4</sub>, PbSO<sub>4</sub>, HgS, Prussian blue, CaF<sub>2</sub>, SnS<sub>2</sub> (mosaic gold), SiO<sub>2</sub>, many silicates, fused PbCrO<sub>4</sub>, and the strongly-ignited oxides: Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>.\** TiO<sub>2</sub>, SnO<sub>2</sub>, and Sb<sub>2</sub>O<sub>3</sub> can be dissolved by long continued boiling with concentrated hydrochloric acid.

*Of the salts insoluble in acids, the following dissolve in aqua regia: PtCl<sub>2</sub>, AuCl, HgS, Sb<sub>2</sub>O<sub>3</sub>, SnS<sub>2</sub>, and Prussian blue (after long treatment).*

*The following substances are not dissolved by aqua regia: AgCl, AgBr, AgI, AgCN, BaSO<sub>4</sub>, SrSO<sub>4</sub>, PbSO<sub>4</sub>, CaF<sub>2</sub>,† fused PbCrO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, native TiO<sub>2</sub> (rutile, anatase, brookite), native SnO<sub>2</sub> (cassiterite, tinstone), SiO<sub>2</sub>, Si, many silicates, C, carborundum, and strongly-ignited iridium (rhodium, ruthenium, and osmium).*

In order to bring such substances in solution it is necessary to subject them to a special treatment. The process to be chosen depends largely upon the nature of the insoluble substance, so that

\* The oxides of antimony are changed to Sb<sub>2</sub>O<sub>4</sub> after long ignition in the air.

† Calcium fluoride will be dissolved by the long continued action of aqua regia.

a few general tests are necessary before going farther. Very often the preliminary examination will have been sufficient, but it is always well to perform the following simple experiments:

1. A small portion of the residue is heated on the charcoal stick to see whether a metallic button can be produced.

(a) No metallic button is produced. The absence of silver, lead, and tin is thereby assured.

(b) A metallic button is formed. The button is flattened in an agate mortar, and its solubility in acids is tested.

(a) The metal dissolves in nitric acid forming a clear solution, showing the absence of tin. A little hydrochloric acid is added to the nitric acid solution; a curdy precipitate is formed if the metal is silver, consisting of silver chloride, insoluble in water, but soluble in ammonia.

If the nitric acid solution becomes turbid on the addition of sulphuric acid, lead is present.

(β) The metal does not dissolve in nitric acid forming a clear solution, but leaves a white, insoluble powder: metastannic acid. A new button is treated with concentrated hydrochloric acid, when it will completely dissolve if silver is absent. Mercuric chloride produces a white precipitate of mercurous chloride in the hydrochloric acid solution: tin is present.

2. A second portion of the residue is heated in a small test-tube with concentrated sulphuric acid and tested to see whether the escaping gas renders a drop of water turbid.

A turbidity shows the presence of an insoluble fluoride ( $\text{CaF}_2$ ).

3. Still another portion of the residue is heated (with the help of a platinum wire) in the upper reducing flame of the gas-burner, allowed to cool in the inner mantle, moistened with dilute hydrochloric acid, and it is noticed whether the odor of hydrogen sulphide is given off. It is then tested to see whether it will now impart a characteristic coloration to the flame. The presence of a sulphate is betrayed by the odor of hydrogen sulphide, and the flame test shows whether barium alone or a mixture of barium, calcium, and strontium is present.

4. Another portion of the residue is tested in the salt of phosphorus bead; silicic acid or a silicate usually gives a skeleton bead (cf. page 410).

As the skeleton bead is not always obtained even when silica is



present, a further test for silicic acid is often necessary. For this purpose a small portion of the substance is mixed with a little calcium fluoride (itself free from silicate), treated with concentrated sulphuric acid and warmed gently on platinum. The evolution of a gas which causes a drop of water to become turbid shows the presence of silicic acid.

5. The salt of phosphorus bead is now heated in the reducing flame to test for the presence of titanium, which causes the bead to become violet. The violet color appears more quickly on the addition of a little piece of tin-foil. If iron is present at the same time, as is always true in the case of rutile, the bead is colored brownish red in the reducing flame.

6. The presence of chromium is often detected by the green color of the residue. In the case of chromite (gray or black residue) a portion is fused with sodium carbonate and potassium nitrate in the platinum spiral (cf. page 108), when a yellow melt is obtained if chromium is present, which yields a reddish-brown precipitate with silver nitrate (after being dissolved in water and acidified with acetic acid) of silver chromate.

7. If the residue is gray or black, it may also consist of carbon. A small portion is heated upon a piece of platinum-foil, when the mass will glow and leave a lighter-colored ash if carbon is present. In doubtful cases a little potassium chlorate is melted in a test-tube, and a little of the residue is added, when a distinct glowing or a little explosion will take place if carbon is present. It is necessary to avoid the addition of shreds of filter-paper in this test.

8. Silicon and silicides (carborundum, etc.) are seldom met with, and show the greatest stability toward the above mentioned reagents. By fusing with caustic alkali in a silver crucible, however, they are readily decomposed with evolution of hydrogen.

After dissolving the melt in water and acidifying, gelatinous silicic acid separates out, particularly after evaporation.

#### METHODS FOR GETTING SUBSTANCES INTO SOLUTION WHICH ARE INSOLUBLE IN ALL ACIDS.

1. **Insoluble Halogen Compounds** (the silver compounds alone come into consideration) can be brought into solution by melting the mass, and by adding a little dilute sulphuric acid, and a piece of zinc so that it comes in contact with both the acid and the insoluble substance. After a while the acid is poured off; it contains the

halogen acid in the presence of zinc sulphate, and is kept for the subsequent acid test, cf. page 300. The residue consists of metallic silver. It is washed with water, dissolved in dilute nitric acid, filtered from any sulphate, silicate, etc., and the solution tested for silver with hydrochloric acid.

2. **Insoluble Sulphates of the Alkaline Earths** are brought into solution by fusing in a platinum crucible with 4-5 times as much calcined sodium carbonate, or with a mixture of equal parts of sodium and potassium carbonates. The finely-powdered substance is mixed in the crucible with the sodium carbonate, the mixture is covered with a thin layer of more carbonate, the crucible is covered and heated at first over a small flame in order to drive off the moisture which the carbonate always contains; after which the temperature is raised until the mass fuses to a thin liquid, this temperature being maintained for about a quarter of an hour. The glowing crucible is then plunged into some cold distilled water, and the fused mass will usually contract so that it can be readily loosened from the sides of the crucible. The mass is warmed with a little water on the water bath until it disintegrates, and no more hard lumps can be felt with a glass rod, when it is filtered. The filtrate will contain the sulphate as sodium sulphate, and the residue will now consist of carbonates of the alkaline earths. It is washed a few times with strong soda solution, then with a 5 per cent. soda solution until no more sulphuric acid can be detected in the filtrate. It is finally washed with hot water until the wash-water no longer reacts alkaline (cf. page 75), dissolved in nitric acid, and analyzed as described on page 76.

3. **Lead Sulphate** is boiled with a concentrated soda solution, filtered and washed first with soda solution, and then with water. Calcium sulphate is also decomposed completely by boiling with soda solution, as is strontium sulphate (though less readily), but barium sulphate is only incompletely decomposed.\*

4. **Silicic Acid and Silicates** should be fused with sodium carbonate, exactly as described on page 407.

5. **Metastannic Acid**, as obtained by the oxidation of tin with nitric acid, is readily dissolved by boiling with a little concentrated

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\* Lead sulphate dissolves readily in hot ammonium acetate solution (conveniently prepared by adding acetic acid, sp. gr. 1.04, to ammonia, sp. gr. 0.96, until the solution no longer reacts alkaline). This solution gives lead sulphide on adding ammonia and ammonium sulphide, lead chromate on adding potassium chromate solution, and lead sulphate on adding a little sulphuric acid. It shows the presence of sulphuric acid by giving a precipitate with barium chloride.

hydrochloric acid, and then treating with considerable cold water (cf. page 250).

Tin dioxide, as it occurs in nature (tinstone), as well as the strongly ignited metastannic acid, cannot be brought into solution in this way. One of the methods mentioned on page 254 (usually the sodium carbonate and sulphur method) must be used.

6. **Insoluble Fluorides** are first heated with concentrated sulphuric acid, and the sulphate formed is brought into solution by the method described on page 425, 2.

7. **Titanium Dioxide** is fused with potassium pyrosulphate in a platinum crucible (cf. pages 94 and 129); or it is fused with sodium carbonate, the melt treated with cold water, and the residue dissolved in hydrochloric acid (cf. page 133).

8. **Chromium Trioxide** and **Chromite** are fused with sodium carbonate and a little potassium nitrate (cf. page 108).

9. **The Insoluble Complex Cyanides** are completely decomposed by boiling with caustic soda in a porcelain dish.

After boiling with the alkali, the product is diluted with water and filtered. The filtrate will contain the acid in the form of its sodium salt; and, in some cases, may also contain aluminium and zinc. The filtrate, therefore, is saturated with carbon dioxide, boiled and any precipitate ( $\text{Al}(\text{OH})_3$  or  $\text{ZnCO}_3$ ) is filtered off; it is dissolved in hydrochloric acid and tested for zinc and aluminium. The alkaline filtrate obtained above is acidified with hydrochloric acid and tested for ferrocyanic and ferricyanic acids according to pages 310 and 313.

The soluble complex cyanides are decomposed before the analysis by heating them with concentrated sulphuric acid (cf. page 123).

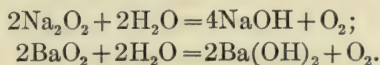
#### SOLUTION OF THE SUBSTANCE.

When a substance is dissolved, whether in water or in acids, phenomena are often observed which may be of great importance as concerns the subsequent analysis. Moreover, the color, reaction of the solution towards indicators, or the evolution of gases will lead to important conclusions. The substance is first tested with regard to its solubility in water, by taking about  $\frac{1}{2}$  gram of its fine powder, adding a little cold water, and noticing whether any bubbles of gas are given off.

A gas is evolved when there is present:



(a) **Peroxides of the Alkalies or Alkaline Earths,\*** which are partly decomposed into hydroxide and oxygen:



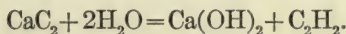
The escaping gas is tested for oxygen by means of a glowing splinter.

In the alkaline solution (red litmus is changed to blue) some undecomposed peroxide will still be found.

The solution is diluted considerably with water, cooled, and carefully acidified with sulphuric acid, a few cubic centimeters of ether and a little potassium dichromate solution added, and the mixture shaken. If a peroxide is present, the upper ether layer will now be colored blue. A still better method for detecting the hydrogen peroxide, formed by the action of the sulphuric acid upon the peroxide, consists in adding a few drops of titanium sulphate solution; a distinct yellow color will be noticed if only traces of hydrogen peroxide are present (cf. pages 53 and 131).

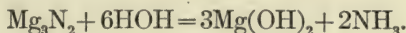
(b) **Carbides of the Alkaline Earths** (calcium carbide).

These are decomposed into acetylene (which has a peculiar odor, and burns with a luminous flame) and calcium hydroxide:



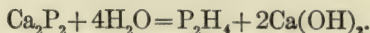
(c) **Nitrides of the Alkaline Earths** (magnesium nitride).

Magnesium nitride is decomposed by water into magnesium hydroxide and ammonia:



If considerable water is added, there is no gas evolution, because the ammonia will be absorbed by the water; but on boiling the solution, ammonia will be given off, which can be readily recognized by its odor.

(d) **Phosphides of the Alkalies and Alkaline Earths.**—These are decomposed by water, setting free spontaneously-combustible phosphine:

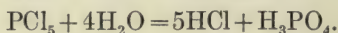



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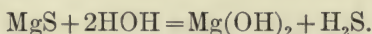
\* Barium peroxide reacts in this way only on warming.

Very small quantities of the phosphide can be recognized by the characteristic garlic odor.

(e) **Many Chlorides, Bromides, and Iodides of the Negative Elements**, *e.g.*  $\text{PCl}_3$ ,  $\text{PCl}_5$ , etc., are decomposed into the halogen hydride and the oxygen acid of the negative element:



(f) **A few Sulphides which are seldom met with** ( $\text{MgS}$ ,  $\text{Al}_2\text{S}_3$ , etc.).—These are decomposed by water with loss of hydrogen sulphide, which can be detected by its odor, and by its blackening lead acetate paper:



After any reaction caused by the first addition of water is over, about 10–15 c.c. more are added, the water is heated to boiling and allowed to cool.

If the substance dissolves completely, forming a clear solution, it is evident that it is unnecessary to test for any insoluble substances in the subsequent analysis.

If a residue remains, it is possible that a part of the substance has dissolved in the water. To determine whether this is the case, the liquid is decanted through a filter, and a few drops are carefully evaporated to dryness on platinum-foil (or a watch-glass). If the foil is heated too hot, volatile compounds may escape unnoticed. If a residue remains after evaporation, it is evident that a part of the original substance is soluble in water. The original residue is then treated several times with small amounts of water, and the aqueous extract thus obtained is analyzed by itself. The part remaining undissolved is now treated with acid; hydrochloric acid being usually used (unless the preliminary examination has shown the presence of either lead or silver, when nitric acid should be used).

The solution in acid is best effected by treating the residue with  $\frac{1}{2}$ –1 c.c. of concentrated acid (it being noticed whether there is any evolution of a gas), warming, and then diluting with water, to dissolve any chlorides insoluble in hydrochloric acid. It must be remembered, however, that bismuth and antimony salts form insoluble basic chlorides on dilution with water, so that too much water should not be added.

If a residue remains after treatment with acid, it is brought into solution by one of the methods described on pages 424 *et seq.*

## II. EXAMINATION FOR THE METALS (CATIONS).

The different solutions are analyzed separately according to the table on pages 430, 431.

## NOTES ON THE GENERAL TABLE FOR THE EXAMINATION AND SEPARATION OF THE GROUPS.

1. *Introduction of Hydrogen Sulphide.*—The acid solution (usually about 50–100 c.c. in volume) is placed in an Erlenmeyer flask of about 300 c.c. capacity, which is provided with a double-bored stopper. Through one of the holes a right-angled piece of glass tubing is introduced so that it just reaches the lower surface of the stopper, while through the other hole another right-angled glass tube is fixed so that it almost reaches the bottom of the flask. The longer tube is raised till it does not touch the liquid, and the solution is heated to boiling, a strong stream of water vapor coming out through both of the tubes. The longer tube is then connected with a Kipp  $\text{H}_2\text{S}$ -generator by means of a rubber tube which is already filled with hydrogen sulphide gas. The apparatus is arranged so that the gas from the generator passes first through a flask filled with water, and then through a tube filled with cotton (to remove any liquid which may be mechanically carried over from the wash-bottle). A steady stream of hydrogen sulphide is conducted through the apparatus, the flame is removed from under the flask, and the shorter tube is closed by means of a piece of rubber tubing which contains a solid glass rod. The longer tube is introduced into the liquid, the flask is shaken well for a few minutes and allowed to cool somewhat. The short tube is then opened, the stopcock of the generator is closed, and an equal volume of cold distilled water is added.\* The solution is again saturated with hydrogen sulphide, the short tube is once more closed and the contents of the flask well shaken for two or three minutes, after which time the precipitation is complete and the precipitate can be immediately filtered off.†

If the preliminary examination has shown that oxidizing substances are present (cf. page 9) or arsenic acid, it is best to reduce

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\* Cf. page 206. Separation of Hg, Pb, etc., from previous groups.

† Cf. Gräbe, Ber., 31, 2981 (1898).



TABLE VII.  
GENERAL TABLE FOR THE EXAMINATION AND SEPARATION OF THE GROUPS.

The solution is treated with hydrochloric acid until no more precipitation takes place, warmed gently, and filtered.

PRECIPITATE.		FILTRATE (can contain all of the remaining metals).	
<p>Hydrogen sulphide is conducted into the solution (which should contain 10–15 c.c. of double normal acid to every 100 c.c. of solution) until it is saturated.† it is diluted with an equal volume of water, more hydrogen sulphide led into it, and then filtered.</p>		<p>FILTRATE (can contain the metals of Groups III and IV in the presence of the alkalis).</p>	
PRECIPITATE.		FILTRATE (can contain the metals of Groups III and IV in the presence of the alkalis).	
<p>White</p> <p>This precipitate is examined according to Table VIII.</p> <p><math>\text{AgCl}</math> <math>\text{Hg}_2\text{Cl}_2</math>, <math>\text{PbCl}_2</math>, <math>(\text{TiCl})^*</math></p>		<p>The filtrate is freed from <math>\text{H}_2\text{S}</math> by boiling, 2 c.c. of concentrated <math>\text{HNO}_3</math> are added, and the solution evaporated to a small volume. A small portion is now taken, an excess of ammonium molybdate added, and the mixture warmed gently; a yellow precipitate shows the presence of <math>\text{H}_3\text{PO}_4</math>.‡ If the preliminary examination shows the presence of non-volatile organic matter, or of oxalic acid,§ it must be destroyed before the test for <math>\text{H}_3\text{PO}_4</math> is made. For this purpose the filtrate is evaporated to dryness and gently ignited. After cooling, a little concentrated <math>\text{HCl}</math> is added, the solution is boiled, a little water added, and any carbon or silica which may be left is filtered off   A portion of this filtrate is then tested with ammonium molybdate for <math>\text{H}_3\text{PO}_4</math>. According to whether phosphoric acid is present or not, the method A or B is used.</p>	
<p><math>\text{HgS}</math>, black <math>\text{PbS}</math>, black <math>\text{Bi}_2\text{S}_3</math>, brown <math>\text{CuS}</math>, black <math>\text{CdS}</math>, yellow or orange</p> <p>insoluble in <math>(\text{NH}_4)_2\text{S}_4</math>.</p>		<p><math>\text{As}_2\text{S}_3</math>, yellow <math>\text{As}_2\text{S}_5</math>, yellow <math>\text{Sb}_2\text{S}_3</math>, orange <math>\text{Sb}_2\text{S}_5</math>, orange <math>\text{SnS}</math>, brown <math>\text{SnS}_2</math>, yellow</p> <p>Soluble in <math>(\text{NH}_4)_2\text{S}_2</math> and <math>\text{Na}_2\text{S}_2</math></p> <p><math>\text{AuS}</math>, black <math>\text{PtS}</math>, black <math>\text{MoS}_3</math>, brown <math>\text{SeS}</math>, orange <math>\text{TeS}</math>, black</p>	

This precipitate is examined according to Table IX.

A. Phosphoric Acid is Absent.		B. Phosphoric Acid is Present.	
The filtrate is diluted to about 100 c.c. with water, $\text{NH}_3$ is added until the solution reacts alkaline, and then colorless $(\text{NH}_4)_2\text{S}$ until no further precipitation takes place.		The filtrate is evaporated to dryness, 10 c.c. of concentrated $\text{HNO}_3$ are added, the solution is again evaporated to dryness, and this process is repeated once more. 10 cc. of concentrated $\text{HNO}_3$ and little by little about 1 gram of tin foil are added, the liquid boiled in a small volume, poured into a narrow cylinder, and allowed to stand quietly over night. In the morning the liquid is siphoned off and is now free from $\text{H}_3\text{PO}_4$ . It is saturated with $\text{H}_2\text{S}$ in order to precipitate Pb, Cu, etc. (which are almost always present with the tin as impurities), and filtered.	
PRECIPITATE.		PRECIPITATE. FILTRATE.	
Can contain $\text{Fe}_2\text{S}_3$ , black $\text{FeS}$ , black $\text{NiS}$ , black $\text{CoS}$ , black $\text{MnS}$ , flesh color $\text{ZnS}$ , white $\text{Al}(\text{OH})_3$ , white $\text{Cr}(\text{OH})_3$ , green $\text{UO}_2\text{S}$ , brown $\text{Ti}(\text{OH})_3$ , white The precipitate is analyzed according to Table X.	Can contain Ca, Sr, Ba, Mg, and Alkalies. The filtrate is concentrated, HCl added, the solution boiled and the deposited S is filtered off. $\text{NH}_3$ and $(\text{NH}_4)_2\text{CO}_3$ are added, the liquid is heated to boiling and filtered.	Contains the impurities which were introduced with the tin, and should be discarded.	Is examined according to A.
	Can contain $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{CaCO}_3$ , It is examined according to Table XI.	Can contain Mg and the Alkalies. It is analyzed according to Table XII.	

\* Besides these substances, HCl can also precipitate from an alkaline solution:  $\text{SiO}_2$ ,  $\text{WO}_3$ ,  $\text{H}_2$ ,  $\text{SbOCl}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_5$ ,  $\text{As}_2\text{S}_3$ ,  $\text{SnS}_2$ , and others.

† Cf. note 1, page 429.

‡ Cf. note 2, page 432. § Cf. note 3, page 432. ¶ Cf. note 4, page 433. ¶ Cf. page 69, § 2.

these with sulphurous acid before treating with hydrogen sulphide. For this purpose, the weakly acid solution is concentrated as much as possible in an Erlenmeyer flask, 100 c.c. of a saturated sulphurous\* acid solution are added, a stopper is introduced into a flask provided with inlet and outlet tubes, and the solution is boiled for a quarter of an hour; 10 c.c. of concentrated hydrochloric acid are then quickly added, and the boiling is continued while carbon dioxide is being passed into the solution, until the excess of sulphurous acid is completely removed.† The solution is then treated with hydrogen sulphide as above described.‡ In this way a precipitate containing no free sulphur is formed by the hydrogen sulphide.

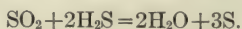
2. The test for phosphoric acid at this place must never be omitted. As is evident from the table, it is desired to separate the members of Group III from those of Group IV by precipitation with ammonia and ammonium sulphide. If phosphoric acid is present in the solution (or oxalic acid) the addition of ammonia can cause the precipitation of calcium, strontium, barium, and magnesium phosphates (or of calcium, strontium, and barium oxalates) with the members of Group III.

It is, therefore, necessary to remove the phosphoric acid before the precipitation with ammonia and ammonium sulphide by evaporation with tin and nitric acid (cf. page 368). In the absence of chromium, the phosphoric acid may be removed by precipitation as basic ferric phosphate (cf. page 365).

3. Oxalic acid is usually detected in the preliminary examination by heating the substance with concentrated sulphuric acid, whereby inflammable carbon monoxide is produced. As, however, formates and other organic substances also give off carbon monoxide on being

\* Ferric salts are not completely reduced by  $\text{SO}_2$  in strongly acid solutions. When they are present, the solution is neutralized with ammonia until a permanent precipitate is formed and then the  $\text{SO}_2$  water is added. It is still better to pass  $\text{SO}_2$  gas into the solution.

† If the  $\text{SO}_2$  were not removed the following reaction would take place:



‡ If Pb, Ba, or Sr salts are present, they will be precipitated as sulphates. In this case the solution is filtered before treating with  $\text{H}_2\text{S}$ , and the precipitate examined by itself for Ba, Sr, and Pb.



treated with concentrated sulphuric acid, this test simply indicates that oxalic acid *may* be present, and is not conclusive. On the other hand, the carbon monoxide is often not detected in the preliminary examination; *e.g.*, if considerable chloride (or other salt) is present causing a gas to be evolved on treatment with concentrated sulphuric acid which does not support combustion. In such a case the carbon monoxide would not burn. If carbon monoxide was not detected in the preliminary examination, and there was no evidence of carbonization, the substance may be tested as follows for oxalic acid: A small portion of the solution is treated with sodium carbonate in a porcelain dish until the solution reacts strongly alkaline, then boiled and filtered. The filtrate is acidified with acetic acid, boiled to drive off carbon dioxide, calcium chloride and ammonia are added, and the solution again acidified with acetic acid; a white crystalline precipitate insoluble in acetic acid shows the presence of oxalic acid. Hydrofluoric acid will give the same test.

4. If carbonization and evolution of vapors with a burnt odor are caused by heating the original substance, the presence of non-volatile organic matter is assured; *e.g.*, tartaric and citric acids, sugar, starch, etc. Such substances prevent the precipitation of aluminium, iron, etc., by means of ammonia and ammonium sulphide (cf. page 92), and consequently must be destroyed by ignition. After ignition, the carbonates or oxides formed are extracted with hydrochloric acid and filtered off. A black carbonaceous residue almost always remains at this point, which is washed well with water, dried, and the carbon completely burned away, when a residue of  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , insoluble in hydrochloric acid, often remains with some silica. This is examined by itself. In order to get it into solution, it should be fused with potassium pyrosulphate (cf. page 94). The metals are then left in the form of soluble sulphates, while the silica remains undissolved, and can be tested according to pages 408 and 423, § 4.

## NOTES ON TABLE VIII.

If the original solution shows an alkaline reaction (with phenolphthaleïn or litmus), a precipitate may be formed on the addition of hydrochloric acid even when none of the metals of the first group are present; in which case the precipitate must be examined by a special method.

Thus a solution of water-glass gives a white, gelatinous precipitate of silicic acid on adding hydrochloric acid, but also on the addition of nitric or sulphuric acid. In the same way, a solution of the alkali tungstates gives a white amorphous precipitate of tungstic acid upon the addition of acids; the precipitate becomes yellow on warming (cf. page 494).

Solutions containing the sulpho salts of arsenic, antimony, and tin are decomposed by the addition of dilute acid, with precipitation of insoluble arsenic, antimony, and tin sulphides.

The water-glass solution can be freed from its silicic acid by evaporation with acid, as described on page 404, and the filtrate analyzed in the usual way for the metals.

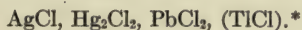
In exactly the same way tungstic acid can be removed from a solution of an alkali tungstate.

If sulpho salts are present, the solution is decomposed by the addition of a dilute acid, and the precipitate is examined according to Table IX, while the solution is tested for alkalies and alkaline earths according to Tables XI and XII.

Only in case non-volatile organic matter is present is it necessary to test the solution for iron and aluminium.

TABLE VIII  
EXAMINATION OF GROUP I.

The precipitate produced by HCl can contain



It is washed with cold water, then boiled with a little water and filtered hot

RESIDUE.	SOLUTION.
Can contain $\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ , and a little $\text{PbCl}_2$ . It is washed with boiling water until the $\text{PbCl}_2$ is all removed, and the residue treated with ammonia on the filter.†	If considerable lead is present, needles of $\text{PbCl}_2$ separate out on cooling. If only a little lead is present, there will be no deposition of $\text{PbCl}_2$ . In all cases the solution is treated with $\text{K}_2\text{Cr}_2\text{O}_7$ solution; a yellow precipitate of $\text{PbCrO}_4$ shows <i>Pb</i> to be present.
RESIDUE.	SOLUTION.
$\text{HgNH}_2\text{Cl} + \text{Hg}$ (black) shows <i>Hg</i> to be present.	Contains $\text{Ag}(\text{NH}_3)_2\text{Cl}$ . It is acidified with $\text{HNO}_3$ ; a white curdy precipitate of $\text{AgCl}$ shows <i>Ag</i> to be present.

\* For the detection of thallium consult the supplement.

† Cf. foot note to page 274.



TABLE IX.

## EXAMINATION OF GROUP II.

The freshly-precipitated sulphides are carefully washed with water containing  $H_2S$ , and the precipitate dried by suction. It is then washed into a porcelain dish, covered with yellow  $(NH_4)_2S_{22}$ ,\* warmed a few minutes with constant stirring (long boiling must be avoided) (cf. page 236), and filtered.

RESIDUE can contain  $HgS$ ,  $PbS$ ,  $Bi_2S_3$ ,  $CuS$ ,  $CdS$ .

It is washed first with water containing ammonium sulphide, then with  $H_2S$  water, and the liquid sucked off as much as possible; it is then warmed with nitric acid (sp. gr. 1.2) in a porcelain dish; all of the sulphides dissolve with the exception of  $HgS$ .

This residue is filtered and washed with water.

RESIDUE ( $HgS$ ). This is dissolved in aqua regia, evaporated almost to dryness, water is added, and the deposited sulphur filtered off.	SOLUTION [ $Pb(NO_3)_2$ , $Cu(NO_3)_2$ , $Bi(NO_3)_3$ , $Cd(NO_3)_2$ ]. It is evaporated to a small volume, a few cubic centimeters of dilute $H_2SO_4$ † are added, and the solution evaporated until fumes of sulphuric acid are given off. After cooling, a little water‡ is added and the solution filtered.	SOLUTION [ $CuSO_4$ , $Bi_2(SO_4)_3$ , $CdSO_4$ ]. The solution is saturated with $NH_3$ and filtered.
	RESIDUE ( $PbSO_4$ ). The formation of white $PbSO_4$ indicates $Pb$ to be present.	RESIDUE ( $Bi_2SO_4$ ). The white precipitate should not contain any other metal than bismuth.
	SOLUTION [ $Cu(NH_3)_4SO_4$ , $Cd(NH_3)_4SO_4$ ]. A blue color shows the presence of $Cu$ , $KCN$ is added until the solution is decolorized, and $H_2S$ is con-	SOLUTION [ $As_2S_3 + S$ ]. It is treated, together with the filter, with fuming $HNO_3$ in a covered beaker, until it has completely dissolved and no more brown vapors are given off. The solution is evaporated to a small volume, an excess of $NH_3$ is added, then some "magnesia mixture," and the solution is vigorously stirred. If considerable arsenic is present, a white crystalline precipitate of $MgNH_4AsO_4 + aq$ is immediately formed.
	RESIDUE ( $As_2S_3 + S$ ). The residue, which always contains considerable free sulphur, is boiled with concentrated $HCl$ (1:1) until no more $H_2S$ is given off, when it is filtered.	RESIDUE ( $As_2S_3 + S$ ). The solution is concentrated to a small volume, a few drops are placed on platinum foil and a piece of zinc added, so that it comes in contact with both the platinum and the solution. After a few seconds the zinc is removed and the platinum is examined to see whether a black stain has been formed upon it, showing the presence of antimony. The zinc is again allowed to act upon the solution, until the evolution of hydrogen

SOLUTION [ $As_4(NH_4)_3$ ,  $SbS_4(NH_4)_3$ ,  $SnS_3(NH_4)_2$ ].

The solution is largely diluted with water and  $HCl$  added to acid reaction. It is then boiled, the sulphides allowed to settle, the upper liquid is poured off, and the residue filtered and washed.

For the separation of arsenic, antimony, and tin sulphides, one of the two following methods can be used:

1. The residue, which always contains considerable free sulphur, is boiled with concentrated  $HCl$  (1:1) until no more  $H_2S$  is given off, when it is filtered.

× SOLUTION  
( $SbCl_5$ ,  $SnCl_4$ )

The solution is concentrated to a small volume, a few drops are placed on platinum foil and a piece of zinc added, so that it comes in contact with both the platinum and the solution. After a few seconds the zinc is removed and the platinum is examined to see whether a black stain has been formed upon it, showing the presence of antimony.

The zinc is again allowed to act upon the solution, until the evolution of hydrogen

<p>The filtrate is treated with stannous chloride solution; a white precipitate of <math>Hg_2Cl_2</math>, which becomes gray on further addition of <math>SnCl_2</math>, shows <math>Hg</math> to be present. §</p>	<p>The test is confirmed by the charcoal stick reaction; the formation of a malleable metallic button shows <math>Pb</math> to be present.</p> <p>   A white precipitate of <math>Al(OH)_3</math> or a brown precipitate of <math>Fe(OH)_3</math> is often formed here if the <math>H_2S</math> precipitate was incompletely washed.</p>	<p>duct into the solution; a yellow precipitate shows <math>Cd</math> to be present.</p> <p>Its presence is confirmed by the flame reaction. A little of the filtered and washed precipitate is carefully roasted on an asbestos thread in the upper oxidizing flame, and the oxide coating is produced on a porcelain dish (cf. page 178).</p> <p>If the brown deposit becomes bluish black on being moistened with <math>AgNO_3</math> solution, <math>Cd</math> is present.</p>	<p>The precipitate is only formed after standing some time in case only little arsenic is present. If no precipitate is formed after standing 12 hours, arsenic is absent.</p>	<p>ceases almost entirely, when the solution is washed away with distilled water, being careful to keep the zinc and platinum in contact with one another. The zinc is then removed, scraping off with the foil any tin which may adhere to it, which is dissolved in concentrated <math>HCl</math>, the solution placed in a small test-tube and a few drops of <math>HgCl_2</math> added. A white precipitate finally becoming gray shows <math>Sn</math> to be present.</p>
<p>shows <math>Hg</math> to be present. §</p>	<p>A black precipitate (metallic Bi) shows the presence of <math>Bi</math>.</p>	<p>2. The mixture of the three sulphides and sulphur is warmed with a solution of ammonium carbonate and filtered.</p>	<p>RESIDUE (<math>Sb_2S_3</math>, <math>SnS_{2-4}</math>, <math>S</math>). The residue is dissolved in concentrated <math>HCl</math> and treated as under sub 1 x.</p>	<p>SOLUTION [<math>As_2(NH_4)_3</math> + <math>AsSO_3(NH_4)_2</math>]. The solution is acidified with <math>HCl</math>, whereby yellow arsenic sulphide is precipitated, showing the presence of arsenic. To confirm this, the precipitate is treated with fuming <math>HNO_3</math>, and the arsenic acid precipitated as <math>MgNH_4AsO_4</math>, as described under 1. An ammoniacal solution of <math>H_2O_2</math> is better than fuming <math>HNO_3</math> (cf. page 259).</p>
<p>* Yellow ammonium sulphide is used, because <math>SnS</math> is insoluble in colorless ammonium sulphide (cf. page 245). † If considerable <math>Pb</math> is present, a white precipitate of <math>PbSO_4</math> will appear on the addition of the <math>H_2SO_4</math> to the nitric acid solution. If only a little <math>Pb</math> is present, the precipitate does not appear until the <math>HNO_3</math> has been expelled by evaporation and the solution has been diluted with water (cf. page 188). ‡ Too much water should not be added, as otherwise <math>Bi</math> may be precipitated as basic sulphate (cf. page 190). § In the presence of <math>Au</math>, <math>Pt</math>, and considerable <math>Sn</math> their sulphides will be mixed with the <math>H_2S</math>. The mercury test is then made with a portion of the residue, but the larger part is tested for <math>Au</math>, <math>Pt</math>, <math>Sn</math>, and <math>Pb</math> (<math>PbSO_4</math> being frequently formed by the action of <math>HNO_3</math> on <math>PbS</math>). The dried precipitate is fused with soda and potassium cyanide in porcelain, the melt extracted with water, and the reduced metals are first treated with nitric acid. This dissolves the lead, which is tested for with <math>H_2SO_4</math>. Concentrated <math>HCl</math> is next added to dissolve any <math>Sn</math>, for which the solution is tested. If a gray residue remains, it is dissolved in aqua regia and tested for <math>Au</math> and <math>Pt</math> by adding ammonium chloride evaporating to dryness on the water-bath, taking up the platinum precipitate in a very little water, filtering, and testing for <math>Au</math> with ferrous sulphate. The charcoal stick test is made for <math>Au</math> (cf. page 263).</p>	<p>   A white precipitate of <math>Al(OH)_3</math> or a brown precipitate of <math>Fe(OH)_3</math> is often formed here if the <math>H_2S</math> precipitate was incompletely washed.</p>	<p>2. The mixture of the three sulphides and sulphur is warmed with a solution of ammonium carbonate and filtered.</p>	<p>RESIDUE (<math>Sb_2S_3</math>, <math>SnS_{2-4}</math>, <math>S</math>). The residue is dissolved in concentrated <math>HCl</math> and treated as under sub 1 x.</p>	<p>SOLUTION [<math>As_2(NH_4)_3</math> + <math>AsSO_3(NH_4)_2</math>]. The solution is acidified with <math>HCl</math>, whereby yellow arsenic sulphide is precipitated, showing the presence of arsenic. To confirm this, the precipitate is treated with fuming <math>HNO_3</math>, and the arsenic acid precipitated as <math>MgNH_4AsO_4</math>, as described under 1. An ammoniacal solution of <math>H_2O_2</math> is better than fuming <math>HNO_3</math> (cf. page 259).</p>

TABLE X (A).  
EXAMINATION OF GROUP III.

The precipitate produced by ammonia and ammonium sulphide in the presence of ammonium chloride is washed four times with water containing  $(\text{NH}_4)_2\text{S}$ , three times with pure water, and then treated in a porcelain dish under constant stirring with cold, double-normal hydrochloric acid, until no more hydrogen sulphide is given off, when it is filtered.

RESIDUE  $[\text{CoS}, \text{NiS}]$ .

SOLUTION  $[\text{FeCl}_2, \text{AlCl}_3, \text{CrCl}_3, \text{UO}_2\text{Cl}_2, \text{MnCl}_2, \text{ZnCl}_2 \text{ (traces of NiCl}_2\text{)}]$ .

The well-washed residue is tested in the borax bead. A blue color shows *Co* to be present.

To test for nickel, a small portion is dissolved in a little aqua regia, the solution evaporated just to dryness, dissolved in a little water, and KCN solution added drop by drop until the precipitate first formed redissolves completely; 2 or 3 c.c. of caustic soda solution are then added, and chlorine conducted into the cold solution (cf. page 151). If *nickel* is present, a black precipitate of  $\text{Ni}(\text{OH})_3$  is formed within a few minutes; a better test for nickel is the reaction with dimethylglyoxime. Cf. p. 152.

N.B.—If the bead was brown in the cobalt test, the presence of nickel is thereby assured, and further testing is unnecessary. Small amounts of *Co* may be present. In order to detect this, a considerable amount of the precipitate is dissolved in aqua regia, evaporated

It is evaporated to a small volume, oxidized with 1–2 c.c. of conc.  $\text{HNO}_3$ , NaOH added until strongly alkaline, boiled, diluted with an equal volume of water, and filtered.

RESIDUE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{U}_2\text{O}_7\text{Na}_2, \text{Mn}(\text{OH})_2, \text{ and traces of Ni}(\text{OH})_2]$ .

SOLUTION  
 $[\text{Al}(\text{ONa})_3, \text{Zn}(\text{ONa})_2]$ .

It is washed with hot water, dissolved in as little concentrated HCl as possible, diluted a little with hot water, boiled a few minutes,\* treated with 10 c.c.  $\text{NH}_4\text{Cl}$  solution, precipitated hot with  $\text{NH}_3$  until the latter is present in excess, and filtered as quickly as possible.

It is acidified with HCl,  $\text{NH}_3$  is added in excess, and it is filtered:

RESIDUE SOLUTION  
 $[\text{Al}(\text{OH})_3, [\text{Zn}(\text{NH}_3)_6\text{Cl}_2]$ .

RESIDUE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{U}_2\text{O}_7\text{Na}_2]$ .

SOLUTION  
 $\text{MnCl}_2$  and traces of  $\text{NiCl}_2$ .

This is dissolved in as little concentrated HCl as possible, considerable  $(\text{NH}_4)_2\text{CO}_3$  solution is added, it is heated just to the boiling-point, and filtered.

RESIDUE SOLUTION  
 $\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, [\text{UO}_2(\text{CO}_3)_3(\text{NH}_4)_4]$ .

Test for Iron: A small portion is dissolved in a few drops of HCl, diluted with water, and a few drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  added with

A white gelatinous precipitate shows the presence of *Al*. It is confirmed by the Thénard-blue reaction (cf. page 95).

The solution is acidified with acetic acid and  $\text{H}_2\text{S}$  conducted into it. A white precipitate of  $\text{ZnS}$  shows the presence of *Zn*. It is confirmed by



solution are added; a dark-blue precipitate of Prussian blue shows that  $Fe^{+3}$  is present.

**Test for Chromium:** A second portion of the residue is fused with sodium carbonate and potassium nitrate in a platinum spiral. After cooling, the melt is flattened on a porcelain plate by means of a pestle, dissolved in a little  $H_2O$ , acidified with acetic acid and a few drops of  $AgNO_3$  added; a red precipitate of silver chromate shows that *Cr* is present.

rated just to dryness, dissolved in a little water, a concentrated solution of potassium nitrite added, the solution is acidified with acetic acid and allowed to stand 12 hours. A yellow crystalline precipitate of  $\text{Co}(\text{NO}_2)_6\text{K}_3$  shows  $\text{Co}$  to be present.

A still better test for cobalt is the Vogel reaction (cf. page 159). The solution is neutralized with  $\text{Na}_2\text{CO}_3$ , until a permanent precipitate is formed, considerable ammonium sulphocyanate is added, and also a little amyl alcohol with an equal volume of ether. The mixture is well shaken. The alcohol-ether layer becomes colored blue if *Co* is present.

\* The boiling serves to convert any manganous chloride into manganous chloride. If the boiling were omitted, the greater part, and in some cases all of the manganese would be precipitated by ammonia (cf. behavior of manganous salts toward KOH and  $\text{NH}_3$ , pages 137 and 138).

cases in, or the manganese would be precipitated by ammonia (cf. behavior of manganese salts in water). In order to determine whether the iron was originally present in the ferrous or ferric condition, the aqueous or hydrochloric acid solution of the original substance is tested with  $\text{K}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  (cf. pages 115 and 120). It is, however, sometimes impossible to determine the iron in which form the iron originally was present. Thus if we have a mixture of ferrous sulphate and considerable  $\text{K}_2\text{C}_2\text{O}_4$ , on treatment with water the iron is oxidized and precipitated as basic sulphate, together with a part of the  $\text{C}_2\text{O}_4^{2-}$  as  $\text{Cr}(\text{OH})_3$ ; both substances are soluble in  $\text{HCl}$ , forming  $\text{FeCl}_3$  and  $\text{CrCl}_3$ .

Another example: A mixture of solid stannous chloride and a little ferric chloride is to be analyzed. On dissolving the mixture in hydrochloric acid, the solution contains ferrous, stannous, and stannic chlorides.

HCl and  $K_4Fe(CN)_6$  solution is added; a brown precipitate or coloration shows the presence of  $U$ .

the presence of  
*Mn*. This is confirmed by fusing a little of the Rinn-  
man's green re-  
action (cf.  
page 165).

melt, which yields a green solution, becoming red on addition of acetic acid, shows the presence of  $Mn$ .

\* The boiling serves to convert any manganic chloride into manganous chloride. If the boiling were omitted, and in some cases all, of the manganese would be precipitated by ammonia (cf. behavior of manganous salts toward KOH and  $\text{NH}_4\text{OH}$ , pages 137 and 138). + In order to determine whether the iron was originally present in the ferrous or ferric condition. It is, however, sometimes impossible to determine of the original substance is tested with  $\text{K}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  (cf. pages 115 and 120). It is, however, sometimes impossible to determine in which form the iron originally was present. Thus if we have a mixture of ferrous sulphate and considerable  $\text{K}_2\text{C}_2\text{O}_4$ , on treatment with water the iron is oxidized and precipitated as basic sulphate, together with a part of the  $\text{Cr}$  as  $\text{Cr}(\text{OH})_3$ ; both substances are soluble in  $\text{HCl}$ , forming  $\text{FeCl}_3$  and  $\text{CrCl}_3$ .  $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 4\text{H}_2\text{O} = 3\text{Fe}_2(\text{SO}_4)_3 + 2\text{Cr}(\text{OH})_3 + 2\text{Cr}(\text{OH})_3 + 2\text{KOH}$ .

TABLE X (B). EXAMINATION OF GROUP III.

The precipitate produced by  $\text{NH}_3$  and  $(\text{NH}_4)_2\text{S}$  (in the presence of  $\text{NH}_4\text{Cl}$ ) is washed four times with water containing  $(\text{NH}_4)_2\text{S}$  and three times with pure water; it is then treated with cold, double-normal  $\text{HCl}$  in a porcelain dish (stirring constantly) until no more  $\text{H}_2\text{S}$  is given off, when it is filtered.

RESIDUE  $[\text{CoS}, \text{NiS}]$ .

SOLUTION  $[\text{FeCl}_3, \text{AlCl}_3, \text{CrCl}_3, \text{UO}_2\text{Cl}_2, \text{MnCl}_2, \text{ZnCl}_2 \text{ with traces of } \text{NiCl}_2]$ .

Examined according to Table X (A).

The  $\text{H}_2\text{S}$  is completely removed by boiling, an excess of bromine water is added, the excess is removed by boiling, the solution is poured into a small Erlenmeyer flask, almost neutralized with  $\text{Na}_2\text{CO}_3$  and an excess of  $\text{BaCO}_3$  suspended in water is added. The contents of the flask are well shaken, the flask is corked up, and the precipitate allowed to settle. After standing about an hour the solution is decanted through a filter.

SOLUTION  $[\text{MnCl}_2, \text{ZnCl}_2, \text{BaCl}_2 \text{ and traces of } \text{NiCl}_2]$ .

PRECIPITATE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{Al}(\text{OH})_3, [\text{UO}_2\text{CO}_3]_3\text{Ba}_2, \text{BaCO}_3]$ .

The solution is heated to boiling and the barium completely precipitated by the addition of dilute  $\text{H}_2\text{SO}_4$ . The  $\text{BaSO}_4$  is filtered off. The solution is treated with  $\text{NaOH}$  until it reacts strongly alkaline; it is warmed gently and filtered.

RESIDUE  $[\text{Mn}(\text{OH})_2, \text{Zn}(\text{OH})_2]$ .

SOLUTION  $[\text{Zn}(\text{ONa})_2]$ .

The precipitate is dissolved in  $\text{HCl}$ , boiled, neutralized with  $\text{NH}_3$ , and if  $\text{Ni}$  is present, a few drops of  $\text{KCN}$  solution are added, precipitate of some  $(\text{NH}_4)_2\text{S}$  and boiled; a pink, flesh-colored precipitate shows the presence of  $\text{Mn}$ . It is confirmed by fusing with soda and nitre (cf. Table X (A)).

It is washed with water until the filtrate gives no precipitate with  $(\text{NH}_4)_2\text{S}$ , dissolved in a little dilute  $\text{HCl}$ , the  $\text{Ba}$  precipitated hot with dilute  $\text{H}_2\text{SO}_4$  and filtered. The filtrate is evaporated to a small volume, treated with an excess of ammonium carbonate, heated just to the boiling-point, a little  $\text{NH}_3$  added, and filtered.

RESIDUE  $[\text{Fe}(\text{OH})_3, \text{Cr}(\text{OH})_3, \text{Al}(\text{OH})_3]$ .

SOLUTION  $[\text{UO}_2(\text{CO}_3)_3] (\text{NH}_4)_2^*$ .

It is dissolved in a little dilute  $\text{H}_2\text{SO}_4$ , and a few drops of the solution formed is tested with  $\text{K}_4\text{Fe}(\text{CN})_6$  for  $\text{Fe}$ ; a precipitate or coloration of Prussian blue shows  $\text{Fe}$  to be present. The remainder of the solution is treated with a concentrated caustic soda solution until it reacts distinctly alkaline, a few crystals of  $\text{KMnO}_4$  are added, and the solution boiled. The chromium is by this means oxidized to  $\text{Na}_2\text{CrO}_4$  with deposition of  $\text{MnO}(\text{OH})_2$ . Alcohol is added drop by drop to the hot violet solution until it becomes colorless, when it is diluted with a little water and filtered.

RESIDUE.

SOLUTION  $[\text{Na}_2\text{CrO}_4, \text{Al}(\text{ONa})_3]$ .

$\text{Fe}(\text{OH})_3$  and  $\text{MnO}(\text{OH})_2$  Discarded.

The yellow filtrate is carefully acidified with dilute  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$  is added till it reacts alkaline, and it is then filtered.

RESIDUE  $\text{Al}(\text{OH})_3$ .

SOLUTION  $(\text{Na}_2\text{CrO}_4)$ .

The white precipitate shows  $\text{Al}$  to be present. It is confirmed by the Thénard's blue reaction.

The yellow solution is divided into two parts. The first part is acidified with acetic acid and treated with  $\text{AgNO}_3$  solution; a reddish-brown precipitate of  $\text{Ag}_2\text{CrO}_4$  shows  $\text{Cr}$  to be present. The other part is acidified with dilute  $\text{H}_2\text{SO}_4$ , an excess of hydrogen peroxide is added, and the solution is shaken with ether. The latter is colored blue if  $\text{Cr}$  is present.

Test for uranium as in Table X (A).

\* The solution always contains some chromium, but it does not interfere with the test for uranium.

TABLE XI.

The precipitate produced by ammonia and ammonium carbonate is well washed with hot water, dissolved in as little dilute  $\text{HNO}_3$  as possible, and carefully evaporated in a porcelain dish to dryness. (The residue must on no account be ignited.) A small portion of the dry residue is dissolved in a little water, filtered from threads of filter-paper, and treated with calcium sulphate solution.

- (a) No precipitate is formed; Ba and Sr are absent; Ca is present.
- (b) A precipitate is formed slowly; Ba is absent; Sr, and perhaps Ca, is present.
- (c) A precipitate is formed immediately; Ba is present, and perhaps Ca and Sr.

If the calcium sulphate solution produces no precipitation, only Ca is present, and a further test is unnecessary. If, however, it produces a precipitate, the original residue must be analyzed according to one of the two following methods:

A. The completely dry nitrates are treated with a few drops of absolute alcohol, stirred, and the alcoholic solution filtered through a filter wet with absolute alcohol into a porcelain crucible.

RESIDUE  $[\text{Ba}(\text{NO}_3)_2, \text{Sr}(\text{NO}_3)_2]$ ,  
with perhaps some  $\text{Ca}(\text{NO}_3)_2$ .

SOLUTION  $[\text{Ca}(\text{NO}_3)_2]$   
and traces of  $\text{Sr}(\text{NO}_3)_2$ .

Two to three c.c. of absolute alcohol are poured on the residue, decanted through the filter, and the process repeated three to four times in order to remove all of the  $\text{Ca}(\text{NO}_3)_2$ . The filtrate, which is now free from calcium, is evaporated to dryness, treated with 3 c.c. of concentrated  $\text{HCl}$ , evaporated again to dryness, and the process repeated. The residue of dry chlorides thus obtained is treated with a few drops of absolute alcohol, stirred, and decanted through a filter wet with absolute alcohol.

RESIDUE  $[\text{BaCl}_2, \text{SrCl}_2]$  with perhaps some  $\text{SrCl}_2$ .

The remaining  $\text{SrCl}_2$  is removed by decanting several times with alcohol and the residue is tested in the flame; a yellowish-green flame shows Ba.

The rest of the residue is dissolved in a little water and treated with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and sodium acetate; a yellow precipitate of  $\text{BaCrO}_4$  shows Ba to be present.

The alcoholic solution is evaporated to dryness and the residue tested in the flame. A carmine-red flame shows Sr.

This is confirmed with the spectroscope (cf. chart).

The solution is evaporated to dryness, the residue ignited, moistened with  $\text{HCl}$  and tested in the flame; a brick-red flame shows Ca.

This is confirmed with the spectroscope (cf. chart).

The calcium may also be detected by adding one or two drops of sulphuric acid, the sulphate being insoluble in alcohol.

B. The dry nitrates are treated with  $\frac{1}{2}$ –1 c.c. of concentrated  $\text{HNO}_3$ , stirred well with a glass rod, and filtered through a small asbestos filter by means of suction.

RESIDUE  $[\text{Ba}(\text{NO}_3)_2, \text{Sr}(\text{NO}_3)_2]$ .

SOLUTION  $\text{Ca}(\text{NO}_3)_2$ .

All of the  $\text{Ca}(\text{NO}_3)_2$  is removed by washing with concentrated  $\text{HNO}_3$ , the residue is dissolved by pouring a little water through the filter, evaporated to dryness, a few cubic centimeters of concentrated  $\text{HCl}$  added, and evaporated to dryness. This process is repeated twice more, in order to convert the nitrates completely into chlorides. The dry chlorides are treated with  $\frac{1}{2}$ –1 c.c. of concentrated  $\text{HCl}$ , half as much absolute alcohol is added, and the solution is filtered through asbestos.

RESIDUE  $(\text{BaCl}_2)$ .

SOLUTION  $(\text{SrCl}_2)$ .

The  $\text{SrCl}_2$  is all removed by washing with absolute alcohol and the residue is tested as under A.

This is evaporated to dryness and tested as under A.

It is evaporated to dryness and tested as under A.



TABLE XII.

## EXAMINATION OF GROUP V (Mg and the Alkalies).

The filtrate from the  $(\text{NH}_4)_2\text{CO}_3$  precipitate can contain magnesium and the alkalies, in the presence of considerable amounts of ammonium salts. It is evaporated to dryness, gently ignited in order to expel the ammonium salts, dissolved in a little dilute HCl, and filtered from the carbonaceous residue (cf. page 66). The solution is divided into two parts; one part is used for the Mg test, and the other part for the K and Na tests.

## TEST FOR MAGNESIUM.

The smaller portion of the hydrochloric acid solution is treated with a little  $\text{NH}_3$ , and, in case a precipitate is formed, ammonium chloride is added until the solution is clear. Sodium phosphate is then added, the solution is stirred and saturated with ammonia. A white crystalline precipitate of magnesium ammonium phosphate shows Mg to be present.

## TESTS FOR POTASSIUM AND SODIUM.

The larger part of the hydrochloric acid solution, which is now free from ammonium salts but can contain magnesium,\* is carefully treated with BaCl<sub>2</sub> solution in order to change any sulphate which may be present into chloride, and Ba(OH)<sub>2</sub> is then added, without filtering, until the solution is strongly alkaline. It is then filtered.

## RESIDUE

[Mg(OH)<sub>2</sub>, BaSO<sub>4</sub>].

SOLUTION [NaCl, KCl, BaCl<sub>2</sub>, Ba(OH)<sub>2</sub>].

## Discarded.

Ammonia and ammonium carbonate are added, the solution warmed to render the BaCO<sub>3</sub> crystalline, and filtered. The filtrate will then contain small amounts of barium, owing to the solubility of BaCO<sub>3</sub> in ammonium salts; it is evaporated to dryness, the ammonium salts expelled by gentle ignition, the residue dissolved in a little water, a few drops of ammonium carbonate and ammonia added, then it is warmed and filtered. The filtrate, which is now free from barium, is evaporated to dryness, the small amounts of ammonium salts are expelled, and a small portion of the residue tested to see what color it imparts to the flame.

(a) If the flame is violet, K is present and Na is absent.

(b) If the flame is colored yellow permanently, Na is present. It is observed through cobalt glass; if the flame appears pink, K is also present.

The rest of the residue is dissolved in a little water, the deposited carbon is filtered off, the solution divided into two parts. One part is tested for potassium, and the other part for sodium.

## TESTS FOR POTASSIUM.

1.  $\text{H}_4\text{PtCl}_6$  produces a yellow crystalline precipitate of  $\text{K}_2\text{PtCl}_6$ .

2. Tartaric acid, in the presence of sodium acetate, produces a white crystalline precipitate of  $\text{KHC}_4\text{H}_4\text{O}_6$ .

## TEST FOR SODIUM.

$\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$  produces a white crystalline precipitate.

\* If Mg is absent, the treatment with BaCl<sub>2</sub> + Ba(OH)<sub>2</sub> should be omitted. The analysis is started at 4.

## EXAMINATION FOR THE NEGATIVE ELEMENTS (ANIONS).

The tests for the acids (anions) are always made after the analysis for the metals (cations), for the preliminary examination (heating in the closed tube and with dilute and concentrated sulphuric acid) and the solubility, combined with the knowledge of the metals that are present, suffice to tell us what acids may and what acids cannot be present.

In order to avoid side-reactions, the acids are first obtained in the form of the neutral alkali salts before proceeding to test for them.

## PREPARATION OF THE SOLUTION FOR THE ANALYSIS FOR ACIDS.

Two cases can be distinguished:

**A. The original substance contains no heavy metal (i.e., only alkalis or alkaline earths are present).**

(a) The substance is soluble in water.

The solution is tested with litmus paper to see whether it is acid, alkaline, or neutral.

**An Alkaline Reaction** shows the possible presence of alkali cyanides, alkali nitrites,\* borates, tertiary phosphates, alkali sulphides, sulpho salts of the alkalis, alkali silicates, etc.

**An Acid Reaction** is shown by many acid salts.

The solution is divided into two parts. If it is neutral, it is analyzed directly for the acids; if it is alkaline half of it is exactly neutralized † with acetic acid and the other half with nitric acid; if it is acid, it is neutralized with sodium carbonate solution.

(b) The substance is insoluble or very difficultly soluble in water, but readily soluble in dilute acids. In this case only the acids of Groups III and IV need be tested for.

The dry substance is boiled with a little concentrated sodium carbonate solution and filtered. The filtrate contains all the acids in the form of their sodium salts, with the exception of phosphoric acid, which has already been tested for in the analysis for the metals.

The solution is now neutralized with dilute nitric acid.

(c) The substance is insoluble in water and in dilute acids.

The following substances may be present:  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $(\text{CaSO}_4)$ ,

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\* Entirely pure alkali nitrites are neutral. The alkaline reaction of the commercial salts is due to the presence of alkali oxide, or silicate.

† Sulphosalts, silicates, stannites, stannates, aluminates, molybdates, tungstates, etc., will yield precipitates at this point which must be examined according to Table XIII.

$\text{CaF}_2$ , and silicates, which often contain  $\text{H}_3\text{PO}_4$ ,  $\text{HBO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ , and  $\text{HCl}$ .

The substance is fused with sodium carbonate in a platinum crucible, extracted with water, and the aqueous solution thus obtained is used for the analysis for acids, after being neutralized.

If the substance is partly soluble in water and in acids, it is first treated with water and then with soda solution, while the residue is fused with sodium carbonate. The three solutions thus obtained are analyzed separately.

**B. The substance contains heavy metals.**

(a) **It is Soluble in Water** or in dilute acids, and contains no non-volatile organic matter (no carbonization in the closed-tube test).

The solid substance is treated with sufficient concentrated soda solution to make the resulting solution weakly alkaline, and filtered. If ammonium salts are present, it is first boiled with the solution of sodium carbonate until the vapors from the solution no longer smell of ammonia, when it is filtered.

The resulting solution is divided into two parts, one part being acidified with acetic acid, and the other with nitric acid.

(b) **The Substance is soluble in Water or Dilute Acids and Contains Non-volatile Organic Matter.**—If metals of the ammonium sulphide and hydrogen sulphide groups are both present, hydrogen sulphide is conducted into the weakly acid solution until it is saturated, the precipitate is filtered off, ammonia is added to the filtrate until it is slightly alkaline, it is filtered again, and this last filtrate is acidified with acetic acid and evaporated to a small volume. The deposited sulphur is filtered off, the solution treated with solid potassium carbonate, filtered if necessary, carefully acidified with nitric acid, vigorously stirred, and if any acid potassium tartrate is formed, it is filtered off and tested as described under tartaric acid. The filtrate is tested for the remaining acids.

(c) **The Substance is Insoluble in Strong Acids.**—Besides the salts mentioned under A (c), the following may be present:  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgCN}$ ,  $\text{PbSO}_4$ , silicates (ferro- and ferri-cyanides).

If silver is present, the halogen acids must be looked for. The insoluble silver salt is reduced by zinc and sulphuric acid, the residue filtered off, and the filtrate examined according to Table XV for  $\text{HCl}$ ,  $\text{HI}$ ,  $\text{HBr}$ , and  $\text{HCN}$ .



TABLE XIII.  
THE SILVER NITRATE TEST.

The original neutral, aqueous solution, or the solution which is acid with acetic or nitric acid, is treated with an excess of silver nitrate.

No PRECIPITATE  
IS FORMED.

A PRECIPITATE IS FORMED.

All acids of  
Groups I, III,  
and IV are ab-  
sent (cf. page  
276).

If the solution was very concentrated, the precipitate may be the silver salt of  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{HNO}_2$ , or  $\text{H}_2\text{SO}_4$ . It is, therefore, treated with water and warmed.

THE PRECIPITATE  
DISSOLVES.

THE PRECIPITATE REMAINS UNDISSOLVED.

All acids of  
Groups I, III,  
and IV are ab-  
sent.

Acids of Groups  
I, III, and IV  
dilute nitric acid.  
THE PRECIPITATE  
DISSOLVES.

The precipitate is warmed with

THE PRECIPITATE DOES NOT DISSOLVE.

One or more  
acids of Groups  
III and IV is pre-  
sent.

The acids of  
Group I are ab-  
sent.

Present: Acids of Group I.

The precipitate is filtered off and the filtrate treated drop by drop with dilute ammonia.

A TURBID ZONE IS FORMED. NO TURBID ZONE IS FORMED

Present: Groups \* III or IV.  
Yellow zone,  $\text{Ag}_3\text{AsO}_3$ ,  $\text{Ag}_3\text{PO}_4$   
Red "  $\text{Ag}_2\text{CrO}_4$   
Brown "  $\text{Ag}_3\text{AsO}_4$ †  
White " silver salts of  $\text{H}_2\text{SO}_4$ ,  
 $\text{H}_2\text{C}_2\text{H}_3\text{O}_6$ ,  $\text{H}_2\text{C}_2\text{O}_4$ ,  $\text{HPO}_3$ ,  $\text{H}_2\text{P}_2\text{O}_7$

Absent: Groups III  
and IV.

\* Boric acid would not be precipitated in case the free acid were neutralized with ammonia. It must be tested for separately.

† It must not be forgotten that  $\text{NH}_3$  produces a brownish precipitate of  $\text{Ag}_2\text{O}$  in silver solutions; in case the zone appears brown, the solution is gently shaken, whereby the turbidity disappears; more  $\text{NH}_3$  is added, and with a little experience it can be determined whether the turbidity is  $\text{Ag}_2\text{O}$  or  $\text{Ag}_3\text{AsO}_4$ .

TABLE XIV.

## THE BARIUM CHLORIDE TEST.

The original, aqueous, neutral solution, or the solution neutralized with acetic acid, is treated with an excess of barium chloride solution.

NO PRECIPITATE IS FORMED.

A PRECIPITATE IS FORMED.

Absent: All acids of Groups III, IV, and VI.	A little dilute HCl is added and the solution warmed.* THE PRECIPITATE DISSOLVES.      THE PRECIPITATE REMAINS.
Absent: Group VI ( $\text{H}_2\text{SO}_4$ and HF).	Present: Group VI.  The precipitate is filtered off and the filtrate neutralized with pure KOH or NaOH (free from carbonate, etc.).  NO PRECIPITATE IS FORMED.      A PRECIPITATE IS FORMED.
	Absent: Acids of Groups III and IV.      Present: Acids of Groups III and IV.

\* Carbonates, sulphites, and thiosulphates will be destroyed; they must afterwards be tested for specially.

If the insoluble substance contains lead, it is boiled with sodium carbonate solution and filtered; the filtrate is acidified with hydrochloric acid, and tested with  $\text{BaCl}_2$  for  $\text{H}_2\text{SO}_4$ .

If silicates are present,  $\text{H}_3\text{PO}_4$ ,  $\text{HF}$ ,  $\text{HBO}_2$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$  must also be tested for.

In whatever way a solution is prepared, its behavior toward **silver nitrate** and **barium chloride** is determined, in order to ascertain to what groups the acids present belong.

After this is determined, the different tests for the individual members are made.

TABLE XV.

## EXAMINATION OF GROUP 1.

$\text{HCN}$  is first tested for, by placing a little of the solution on a watch-glass, adding a few drops of yellow ammonium sulphide, evaporating carefully to dryness, acidifying the dry mass with  $\text{HCl}$ , and adding a drop of  $\text{FeCl}_3$  solution. If a blood-red coloration is produced,  $\text{HCN}$  is present, in which case a larger portion of the neutral solution is treated with nickel sulphate \* solution in excess, and filtered.

## PRECIPITATE

## SOLUTION.

$\text{Ni}(\text{CN})_2$ Discarded.	The solution, which is now free from hydrocyanic acid, is treated with a little caustic soda solution (free from halogen), boiled, and the precipitate of $\text{Ni}(\text{OH})_2$ filtered off. The filtrate is divided into two parts, one part being used for the $\text{HBr}$ and $\text{HI}$ tests and the other for the $\text{HCl}$ test.	
	Tests for $\text{HI}$ and $\text{HBr}$ .	Test for $\text{HCl}$ .
	The solution is acidified with dilute $\text{H}_2\text{SO}_4$ , chlorine water is added drop by drop, and the solution is shaken with $\text{CS}_2$ or $\text{CHCl}_3$ . If the latter is colored violet, $\text{HI}$ is present. By further addition of chlorine water, the $\text{CS}_2$ or $\text{CHCl}_3$ is decolorized completely if $\text{HBr}$ is absent, but turned yellowish-brown if $\text{HBr}$ is present. If too much chlorine water is used a wine-yellow color is produced.	The solution is slightly acidified with $\text{HNO}_3$ , and precipitated by the addition of dilute $\text{AgNO}_3$ drop by drop. $\text{AgI}$ and $\text{AgBr}$ are first precipitated (yellow). This is filtered off, and more $\text{AgNO}_3$ is added. If the precipitate still appears yellow, it is filtered through a new filter, and $\text{AgNO}_3$ is again added to the filtrate until a white precipitate of $\text{AgCl}$ is formed if $\text{HCl}$ is present.

\* If hydroferricyanic acid is present a little ferrous sulphate is also added. Hydroferrocyanic acid is completely precipitated by nickel sulphate.



## GROUP II.

The members of this group are almost always detected in the preliminary examination. The special tests for these acids are described on page 319 *et seq.*

## GROUP III.

$\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{C}_2\text{O}_4$  are recognized in the preliminary examination.  $\text{HPO}_3$ ,  $\text{H}_4\text{P}_2\text{O}_7$ ,  $\text{HBO}_2$ , and  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  are tested for separately by the special reactions described on page 336 *et seq.*

## GROUP IV.

$\text{CrO}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{H}_2\text{S}_2\text{O}_3$  are detected in the preliminary examination, and in the analysis for metals.

## GROUP V.

$\text{HClO}_3$  and  $\text{HNO}_3$  are usually detected in the preliminary examination. Their presence is, however, always confirmed by the procedure described on page 387.

## GROUPS VI AND VII.

These acids are usually detected in the preliminary examination. Their presence is confirmed by the tests described under  $\text{H}_2\text{SO}_4$ ,  $\text{HF}$ , and  $\text{SiO}_2$ .

## B. THE SUBSTANCE IS A METAL OR AN ALLOY.

The analysis of a metallic alloy is much simpler than that of a mixture of salts, because there are no acids to test for. Of the electro-negative elements, usually only phosphorus, silicon, carbon, and sulphur have to be considered.

As all metals, with the exception of gold, platinum, tin, and antimony, are soluble in nitric acid, alloys are usually brought into solution by dissolving therein, and the use of aqua regia is only necessary in a few cases. Many alloys rich in silicon (*e.g.* copper silicide) are extremely difficultly soluble even in aqua regia, and are best brought into solution by fusing with caustic alkali in a silver crucible, and afterwards dissolving the melt in nitric acid.

It is not advisable to dissolve an alloy in hydrochloric acid, for phosphides, carbides, silicides, sulphides, and arsenides, which are often present in small amounts, are decomposed by this acid in such a way that the negative elements are evolved as hydrogen compounds, and thus escape detection. For the analysis of ordinary alloys, the following procedure is used:

One to two grams of the alloy (best in the form of borings) are

placed in a 200 c.c. porcelain dish under a good hood and treated with about 20 c.c. of nitric acid, sp. gr. 1.25–1.30 (1 vol. conc.  $\text{HNO}_3$  + 1 vol.  $\text{H}_2\text{O}$ ). After the first violent reaction is over, the acid is carefully evaporated (with constant stirring) almost to dryness, being careful to avoid overheating;\* a little water is added and warmed.

(a) The mass dissolves completely. The alloy contains neither tin nor antimony; it is analyzed according to Table XVI.

(b) The mass does not dissolve completely, but a white, greenish residue remains; it is analyzed according to Table XVII.

### C. THE SUBSTANCE IS A LIQUID.

The color, odor, and reaction towards litmus enable one to draw important conclusions.

(a) The solution reacts neutral; it contains no free acid, free base, acid salt, no salt which shows an acid or alkaline reaction on account of hydrolysis, nor any insoluble salt.

First of all, it is determined whether there are any solid substances dissolved in the liquid by evaporating a small portion to dryness at as low a temperature as possible (so as not to lose any volatile substances). If a residue remains, it is examined according to A, page 413.

(b) The solution reacts alkaline. An alkaline reaction may be due to the presence of hydroxides of the alkalis or alkaline earths, peroxides, carbonates, borates, cyanides, silicates, sulphides (zincates, aluminates, molybdates, tungstates) of the alkalis, as well as by ammonia or hypochlorites, etc.

If the solution, for example, contains hydroxides or carbonates of the alkalis, it is evident that substances which are precipitated by them cannot be present at the same time, except, in some cases, in the form of complex ions (cyanides, tartrates, etc.).

The solution is at once tested for peroxides, hydroxides, and carbonates, as well as for the sulphides of the alkalis.

To test for peroxides ( $\text{H}_2\text{O}_2$ ) a small portion of the solution is warmed with a few drops of cobalt nitrate solution; a black precipitate shows the presence of  $\text{H}_2\text{O}_2$ .† Or the solution may be tested

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\* Otherwise insoluble basic salts are likely to be formed. If this be the case, as is often shown by the dark color of the residue, a little conc.  $\text{HNO}_3$  is added, the liquid is warmed gently and then diluted with water.

† See foot-note, page 452.

TABLE XVI.

A. The alloy after being evaporated with nitric acid dissolves in water, forming a clear solution. The alloy contains neither tin nor antimony.  
Two c.c. of  $\text{H}_2\text{SO}_4$  are added and the solution evaporated until white fumes of sulphuric acid come off thickly.

RESIDUE.

Can contain Bi, Cu, Cd, Fe, Mn, Ni, Co, Zn, Al, $\text{P}_2\text{O}_5$ . It is saturated with $\text{H}_2\text{S}$ and filtered.	
PRECIPITATE.	SOLUTION.
White $\text{PbSO}_4$ . It is washed with water and the presence of lead confirmed by the charcoal-coal-stick test. A malleable button, soluble in $\text{HNO}_3$ shows $\text{Pb}$ to be present.	$\text{FeSO}_4$ , $\text{MnSO}_4$ , $\text{NiSO}_4$ , $\text{CoSO}_4$ , $\text{ZnSO}_4$ , $\text{Al}_2(\text{SO}_4)_3$ , $\text{H}_3\text{PO}_4$ . The excess of $\text{H}_2\text{S}$ is expelled by boiling, a few drops of concentrated $\text{HNO}_3$ are added to oxidize the iron; then 10 c.c. of $\text{NH}_4\text{Cl}$ solution, and $\text{NH}_3$ solution drop by drop until the boiling liquid smells of $\text{NH}_3$ permanently; the solution is quickly filtered.
PRECIPITATE.	SOLUTION.
$\text{Bi}_2\text{S}_3$ , $\text{CdS}$ , $\text{CuS}$ . It is dissolved in warm, dilute $\text{HNO}_3$ , the deposited sulphur filtered off, an excess of $\text{NH}_3$ added, and filtered.	$[(\text{MnCl}_4)](\text{NH}_4)_2$ , $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ , $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ , $[\text{Zn}(\text{NH}_3)_6]\text{Cl}_2$ . This is saturated with $\text{H}_2\text{S}$ and filtered, the filtrate being rejected *. The precipitate, consisting of sulphides of Mn, Co, Ni, and Zn, is treated with cold dilute $\text{HCl}$ and filtered.
PRECIPITATE.	SOLUTION.
$\text{Bi}(\text{OH})_3$ , white. It is dissolved in a little $\text{HCl}$ and treated with an alkaline solution of $\text{SnCl}_2$ . A black precipitate of $\text{Bi}_2\text{O}_3$ or $\text{Bi}$ shows $\text{Bi}$ to be present.	$[\text{Fe}(\text{OH})_3]$ , $[\text{Al}(\text{OH})_3]$ , $[\text{Al}(\text{Fe})\text{PO}_4]$ . It is dissolved in a little $\text{HNO}_3$ , and a little of the solution tested for Fe by the addition of $\text{K}_4\text{Fe}(\text{CN})_6$ . The formation of Prussian blue shows presence of Fe. Another portion of the solution is tested with ammonium molybdate solution. A yellow crystalline precipitate shows the presence of P. The principal part of the solution is treated with an excess of $\text{KOH}$ and filtered. The filtrate, which may contain any Al as $[\text{Al}(\text{OK})_3]$ , is acidified with $\text{HCl}$ treated with $\text{NH}_3$ . A white, gelatinous precipitate shows the presence of Al.
	$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , $[\text{Cd}(\text{NH}_3)_6]\text{SO}_4$ . A blue-colored solution shows Cu. The solution is decolorized by the addition of $\text{KCN}$ , and $(\text{NH}_4)_2\text{S}$ added. A yellow precipitate of $\text{CdS}$ shows the presence of Cd.
	$\text{NiS}$ , $\text{CoS}$ , examined according to Table X (A). The $\text{H}_2\text{S}$ is boiled off and the solution treated with an excess of $\text{KOH}$ and filtered. RESIDUE. $\text{MnCl}_2$ , $\text{ZnCl}_2$ . SOLUTION. $\text{Zn}(\text{OK})_2$ . Acetic acid is added and $\text{H}_2\text{S}$ conducted into the solution. A green white precipitate of $\text{ZnS}$ shows $\text{Zn}$ to be present.

\* If neither iron nor aluminium were present in the alloy, this filtrate is tested for phosphoric acid. It is evaporated to a small volume, filtered from deposited sulphur if necessary, and tested with ammonium molybdate. If the alloy contains magnesium, it will be present in this filtrate and must be tested for according to page 65, § 4.



TABLE XVII.

B. The alloy, after being evaporated with nitric acid, does not all dissolve in water. The alloy contains tin or antimony, or both.\*  
It is filtered.

RESIDUE.	SOLUTION. <sup>1</sup>
<p><math>\text{SnO}_2</math>, <math>\text{Sb}_2\text{O}_3</math>, (<math>\text{Sb}_2\text{O}_5</math>), <math>\text{P}_2\text{O}_5</math>, <math>\text{Bi}_2\text{O}_3</math>, and traces of Cu, Pb, Fe, etc.</p> <p>It is washed with water, KOH added to alkaline reaction, and then 5-10 c.c. of <math>\text{K}_2\text{S}</math> solution. This is warmed some time on the water-bath and filtered.</p>	<p>Examined according to Table XVI.</p>
<p><math>\text{Bi}_2\text{S}_3</math>, <math>\text{PbS}</math>, <math>\text{CuS}</math>, etc.</p> <p>It is dissolved in <math>\text{HNO}_3</math>, filtered from sulphur, and the filtrate added to the previous solution.<sup>1</sup></p>	<p><math>\text{K}_2\text{SnS}_3</math>, <math>\text{K}_3\text{SbS}_3</math>, <math>\text{K}_3\text{PO}_4</math>.</p> <p>It is diluted with water, acidified with dilute HCl, and filtered.</p> <p>SOLUTION.</p>
<p><math>\text{SnS}_2</math>, <math>\text{Sb}_2\text{S}_3</math>, or <math>\text{Sb}_2\text{S}_5</math>.</p> <p>It is dissolved in concentrated HCl, boiled, diluted with a little water, filtered from deposited sulphur, and tested according to Table IX for Sn and Sb.</p>	<p><math>\text{KH}_2\text{PO}_4</math>, KCl.</p> <p>The solution is evaporated to a small volume, saturated with ammonia and treated with magnesia mixture. A white crystalline precipitate shows <math>\text{H}_3\text{PO}_4</math> or P to be present.<sup>†</sup></p>

\* In the case of many alloys containing silicon (iron and steel), silicic acid separates out on the addition of  $\text{HNO}_3$ . This is usually present in very small amounts, and is detected as described under silicic acid.

† This is confirmed by dissolving the precipitate in  $\text{HNO}_3$  and testing with ammonium molybdate solution.

by adding some titanium sulphate solution and acidifying carefully with cold dilute sulphuric acid; a yellow coloration shows the presence of  $\text{H}_2\text{O}_2$ .†

A still more sensitive reagent, according to Schöne,‡ is a very dilute solution of  $\text{FeCl}_3 + \text{K}_3[\text{Fe}(\text{CN})_6]$ . If the slightest trace of  $\text{H}_2\text{O}_2$  is present in the solution, the red solution becomes greenish, and after a time Prussian blue separates out.

In order to detect the presence of hydroxides and carbonates in the presence of  $\text{H}_2\text{O}_2$ , a portion of the solution is boiled for a long time in a porcelain dish in order to destroy the peroxide, when barium chloride is added until no more precipitate is formed. If the solution then shows an alkaline reaction, the presence of hydroxides§ is assured. If the precipitate produced by barium chloride dissolves in acid with effervescence, and the gas evolved renders barium hydroxide solution turbid, carbonates are present. If the solution smells of ammonia, a small portion is evaporated to dryness in order to see whether other compounds are present, and the residue is examined according to A, page 413.

(c) The solution reacts acid; it can then contain substances which are soluble in water and in acids, as well as free acids. A small portion is evaporated to dryness in order to see whether any non-volatile matter is present. If no residue is obtained, the solution is neutralized with soda and tested for acids. If a residue is obtained, it is examined according to A, page 413.

D. *The substance to be analyzed is a gas.*

This case will be considered in Volume II under Gas Analysis.

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\* If the alkaline solution contains hydrochlorites or sulphides, these will also give a black precipitate with cobalt nitrate; the above reaction serves only to detect  $\text{H}_2\text{O}_2$  in the absence of hypochlorites or sulphides. If the latter bodies are present,  $\text{H}_2\text{O}_2$  cannot be present, because hypochlorites are reduced to chlorides and sulphides oxidized to sulphates by  $\text{H}_2\text{O}_2$ .

The presence of hypochlorites is usually detected by the odor; by acidifying with dilute  $\text{H}_2\text{SO}_4$ , chlorine can be smelled. Sulphides give off  $\text{H}_2\text{S}$  on being acidified. Hypochlorites and sulphides cannot exist together in the same solution.

†  $\text{H}_2\text{O}_2$  can also be detected by the chromic acid reaction, but this test is less certain than that with titanium sulphate.

‡ Ber., 7, 1695.

§ Either as such in the original solution or by hydrolysis of peroxides. This test for OH ions in the presence of carbonates has been used for years by the author. It is reliable, though care must be taken to add an excess of  $\text{BaCl}_2$ , as otherwise an alkaline reaction may be due to  $\text{BaCO}_3$ , which is more soluble in water than in  $\text{BaCl}_2$  solution.

## SUPPLEMENT.

REACTIONS OF SOME OF THE RARER  
METALS.





## REACTIONS OF SOME OF THE RARER METALS.

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IN the treatment of the rare metals, the same method and order will be used as with common metals.

### THE ALKALI GROUP.

CÆSIUM, RUBIDIUM, LITHIUM.

CÆSIUM, Cs. At. Wt. 132.81.

*Occurrence.*—Cæsium and rubidium are not rare elements, strictly speaking, for they are found almost everywhere, but always only in very small amounts. Thus cæsium replaces potassium in many feldspars and micas, and is found in many rocks which carry these minerals, as well as in mineral waters which ooze from them. Cæsium and rubidium were discovered in the mother liquor of Durkheimer brine in the year 1860 by Bunsen and Kirchhoff by means of the spectroscope.

Pollucite, a mineral closely related to leucite, found at Elba and crystallizing in the regular system, is a typical cæsium mineral. Its composition is  $[\text{SiO}_3]_9\text{Al}_4\text{Cs}_4\text{H}_2$ .

Cæsium and rubidium in all their reactions behave almost exactly like potassium. The principal difference between these three metals lies in the different solubilities of their corresponding salts, as will be seen by the table given on page 458.

### REACTIONS IN THE WET WAY.

A solution of cæsium chloride should be used.

1.  $\text{H}_2[\text{PtCl}_6]$  produces a yellow crystalline precipitate which is of a lighter color than the corresponding potassium salt and is much less soluble; 100 parts of water dissolve at  $0^\circ \text{C}$ . only 0.024 part and at  $100^\circ \text{C}$ . 0.377 part of the salt.

2. **Tartaric Acid** produces, as with potassium and rubidium, a white, crystalline precipitate,  $\text{CsHC}_4\text{H}_4\text{O}_6$ ; 100 parts of water dissolve at  $25^\circ \text{C}$ . 9.7 parts, and at  $100^\circ$  97.1 parts of the salt.

3.  $\text{H}_2[\text{SnCl}_6]$  (a solution of  $\text{SnCl}_4$  in concentrated  $\text{HCl}$ ) produces in concentrated solutions a white, crystalline precipitate of  $\text{Cs}_2[\text{SnCl}_6]$  (octahedrons). Ammonium salts give the same reaction, but potassium and rubidium salts do not.

#### REACTIONS IN THE DRY WAY.

Cæsium compounds color the flame reddish violet, very similar to the potassium flame.

*Flame Spectrum.* An intensely blue double line,  $455.5\mu\mu$ ,  $459.3\mu\mu$ . At higher temperatures a number of paler lines appear of subordinate importance; in the red  $697.3\mu\mu$  and  $672.3\mu\mu$ , in the orange yellow  $621.3\mu\mu$  and  $601\mu\mu$ , in the yellow  $584.5\mu\mu$ , in the green  $566.4\mu\mu$ ,  $563.5\mu\mu$ ,  $550.3\mu\mu$ ,  $547.1\mu\mu$ ,  $541.9\mu\mu$ , and  $535.1\mu\mu$ . Moreover, a faint continuous spectrum is seen from the yellow to the blue. See chart.

#### RUBIDIUM, Rb. At. Wt. 85.45.

*Occurrence.*—Rubidium almost always accompanies cæsium and is found in many mineral waters; in carnallite from Stassfurt; in lepidolite,  $\text{Si}_3\text{O}_9\text{Al}_2(\text{Li}, \text{K}, \text{Na})_2(\text{F}, \text{OH})_2^*$ ; in triphylite,  $\text{PO}_4(\text{FeMn})(\text{LiCsRb})$ ; and in spodumene,  $(\text{SiO}_3)_2\text{Al}(\text{LiNa})$  a mineral of the pyroxene group. As far as the author knows, there is no typical rubidium mineral.

#### REACTIONS IN THE WET WAY.

1.  $\text{H}_2[\text{PtCl}_6]$  produces, as with cæsium and potassium salts, a white, crystalline precipitate of  $\text{Rb}_2[\text{PtCl}_6]$ , which is more difficultly soluble than the corresponding potassium salt, but more soluble than the cæsium salt; 100 parts of water dissolve at  $0^\circ \text{C}$ . 0.134 part, and at  $100^\circ$  0.634 part of the salt.

2.  $\text{H}_2[\text{SnCl}_6]$  produces a white precipitate only in very concentrated solutions. The salt is much more soluble than the corresponding cæsium salt, but this reaction is not suitable for separating the two metals.

3. **Tartaric Acid** produces a precipitate of  $\text{RbHC}_4\text{H}_4\text{O}_6$  only in concentrated solutions; 100 parts of water dissolve at  $25^\circ \text{C}$ . 1.18 parts, and at  $100^\circ \text{C}$ . 94.1 parts of the salt. The corresponding cæsium salt is more soluble, while that of potassium is less soluble.

\* Lepidolite from Rozena contains about 0.54 per cent. Rb and 0.0014 per cent. Cs.



## REACTIONS IN THE DRY WAY.

*Flame Coloration.*—Similar to caesium.

*Flame Spectrum.*—Violet double lines  $420.2\mu\mu$  and  $421.5\mu\mu$ , also the red double line  $781.1\mu\mu$  and  $795.0\mu\mu$ . At higher temperatures a continuous spectrum is visible from the yellow to the blue in which the following lines are to be found in addition to those given above; in the orange-yellow  $629.8\mu\mu$ ,  $626.1\mu\mu$ ,  $620.6\mu\mu$ ,  $617.7\mu\mu$  in the yellow-green  $572.4\mu\mu$ ,  $570.0\mu\mu$ ,  $564.8\mu\mu$  and of subordinate importance the green lines  $543.5\mu\mu$ ,  $536.5\mu\mu$ , and  $516.8\mu\mu$ .

## LITHIUM, Li. At. Wt. 6.94.

*Occurrence.*—Lithium is found to a greater extent in nature than caesium and rubidium; in triphylite,  $\text{PO}_4(\text{Fe}, \text{Mn})(\text{Li}, \text{Cs}, \text{Rb})$ ; in petalite,  $\text{Si}_4\text{O}_{10}\text{Al}(\text{Li}, \text{Na}, \text{H})$ , a mineral of the feldspar group (also called castorite); in amblygonite,  $\text{Li}(\text{AlF})\text{PO}_4$ , monoclinic; in lepidolite,  $\text{Si}_3\text{O}_9\text{Al}_2(\text{Li}, \text{K}, \text{Na})_2(\text{F}, \text{OH})_2$ ; in many varieties of tourmaline, and muscovite, in epidote and orthoclase, and consequently in many mineral-spring waters. In some cases as much as 36 milligrams are contained in a liter of spring water.

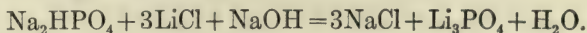
Lithium is the lightest of all metals, and floats on petroleum. It oxidizes quickly in the air, and decomposes water at ordinary temperatures, forming  $\text{LiOH}$ , which dissolves slowly in the water; the solution reacts alkaline and absorbs carbon dioxide from the air with avidity, forming difficultly-soluble  $\text{Li}_2\text{CO}_3$ .

Lithium chloride is soluble, even in the anhydrous state, in a mixture of alcohol and ether as well as in amyl alcohol (difference from the remaining metals of this group).

## REACTIONS IN THE WET WAY.

A solution of lithium chloride should be used.

1.  $\text{H}_2[\text{PtCl}_6]$  produces no precipitation.
2. **Tartaric Acid** produces no precipitation.
3.  $\text{Na}_2\text{HPO}_4$  produces from boiling, moderately-concentrated solutions a white precipitate of tertiary lithium phosphate. The precipitation is only quantitative when the solution is made alkaline with caustic soda, evaporated to dryness, and taken up in water containing ammonia:



Lithium phosphate is fusible (difference from magnesium and the alkaline earths).

4.  $(\text{NH}_4)_2\text{CO}_3$ . If ammonium carbonate and ammonia are added to a concentrated lithium solution, lithium carbonate is precipitated in the form of a white powder. The salt, contrary to the other alkali carbonates, is very difficultly soluble in water: 100 parts of water dissolve at  $13^\circ \text{C}$ . 1.31 parts of  $\text{Li}_2\text{CO}_3$ . In the presence of considerable alkali chloride or of ammonium chloride, no precipitation takes place.

#### REACTIONS IN THE DRY WAY.

*Flame Coloration.*—Pure lithium salts impart a magnificent carmine-red coloration to the gas-flame. If considerable amounts of sodium salts are present at the same time, the lithium flame is completely masked; but if the flame is observed through cobalt glass the red color becomes distinctly visible.

*Flame Spectrum.*—An intensely red line  $670.8\mu\mu$  and at higher temperatures the pale orange-yellow line  $610.3\mu\mu$ .

#### SUMMARY OF THE ALKALI METALS.

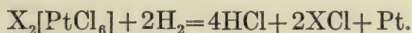
	LITHIUM.	SODIUM.	POTASSIUM.	RUBIDIUM.	CÆSIUM.
At. Wt. ....	6.94	23.00	39.10	85.45	132.81
Melting-point ....	$180^\circ \text{C}$ .	$95.6^\circ \text{C}$ .	$62.5^\circ \text{C}$ .	$38.5^\circ \text{C}$ .	$26-27^\circ \text{C}$ .
Solubility of the $\text{X}_2(\text{PtCl}_6)$ compound in alcohol. ....	readily soluble	readily soluble	insoluble	insoluble	insoluble
Solubility of the $\text{X}_2(\text{PtCl}_6)$ compound in water: 100 parts of water at $20^\circ \text{C}$ . dissolve. ....	considerable	considerable	1.12	0.141	0.079
100 parts of water at $100^\circ \text{C}$ . dissolve. ....	considerable	considerable	5.13	0.634	0.377
Solubility of acid tartrates: 100 parts water dissolve—	—	—	—	—	—
at $10^\circ \text{C}$ .	considerable	considerable	0.425	1.18	9.7
at $25^\circ \text{C}$ .	—	—	—	—	—
Solubility of alums: 100 parts water dissolve at $17^\circ \text{C}$ . ....	—	—	13.5	2.27	0.619
Solubility of the chlorides in alcohol-ether. ....	readily soluble	insoluble	insoluble	insoluble	insoluble
Solubility of the carbonates in absolute alcohol. ....	insoluble	insoluble	insoluble	insoluble	soluble

## DETECTION OF LITHIUM, RUBIDIUM, AND CÆSIUM IN THE PRESENCE OF CONSIDERABLE SODIUM AND POTASSIUM.

The solution containing the metals as chlorides is evaporated almost to dryness, treated with 90 per cent. alcohol (which is well rubbed into the residue) and filtered. The alcoholic solution contains all of the Li, Rb, and Cs, with small amounts of K and Na. It is again evaporated almost to dryness and once more extracted with alcohol.\* This alcoholic solution is now evaporated to dryness, the residue treated with concentrated hydrochloric acid,† again evaporated, gently ignited over the free flame, and, after cooling, the residue is rubbed with ether-alcohol mixture by means of a glass rod, after which the solution is filtered through a filter that is moistened with the ether-alcohol mixture. The filtrate which contains the lithium is evaporated to dryness and then tested for lithium by means of the flame reaction, and in the spectroscope.

The residue insoluble in alcohol-ether is dissolved in a little water, precipitated with chloroplatinic acid and filtered. The precipitate is repeatedly treated with boiling water in a porcelain dish, decanting off the liquid each time through the filter.

First of all, the potassium salt dissolves in the hot water, forming a yellow solution. The treatment with hot water is continued until the residue is of a bright-yellow color. It is then dried, placed in a porcelain boat, and heated in a glass tube made of difficultly fusible glass in a stream of dry hydrogen, whereby the alkali chloroplatinates are reduced to chloride and platinum:



After cooling, the residue is treated with a little water, the platinum filtered off, and the solution is evaporated to dryness and tested in the spectroscope for Cs and Rb.

\* If only traces of the rare alkalies are present, the residue must be extracted several times with alcohol.

† This is done in order to change LiOH into LiCl. Some of the former is formed by evaporating the solution, and it is insoluble in alcohol-ether.



In order to detect lithium, cæsium, and rubidium in a silicate undecomposable by acids (lepidolite, for example) the finely-powdered mineral is decomposed with hydrofluoric and sulphuric acids as described on page 409, the sulphates changed to chlorides by the addition of barium chloride, and the solution freed from other metals as described on page 66 in the case of magnesium, after which the above separation is made.

### METALS OF THE $(\text{NH}_4)_2\text{S}$ GROUP.

BERYLLIUM, ZIRCONIUM, THORIUM, YTTRIUM, ERBIUM  
CERIUM, LANTHANUM, DIDYMIUM, TANTALUM, NIOBIUM.

**BERYLLIUM**, Be. At. Wt. 9.1.

*Occurrence*.—Chrysoberyl,  $(\text{AlO}_2)_2\text{Be}$ ; phenacite,  $\text{SiO}_4\text{Be}_2$ ; beryl,  $\text{Si}_6\text{O}_{18}\text{Al}_2\text{Be}_3$ ; euclase,  $\text{SiO}_5\text{AlBeH}$ ; meliphanite,  $\text{Si}_3\text{O}_{10}\text{FBe}_2\text{Ca}_2\text{Na}$ ; and leucophanite,  $\text{Si}_2\text{O}_6\text{FBeCaNa}$ .

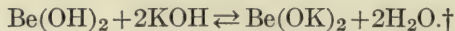
Beryllium is a bivalent metal, and forms a white oxide,  $\text{BeO}$ , which is soluble in acids. Beryllium salts react acid in aqueous solution and possess a sweetish, astringent taste. The element is usually called Glucinum, Gl, in England and the United States.

#### REACTIONS IN THE WET WAY.

A solution of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  should be used.

1. **Ammonia** and **Ammonium Sulphide** produce a white precipitate of  $\text{Be}(\text{OH})_2$ , similar in appearance to  $\text{Al}(\text{OH})_3$ , insoluble in an excess of the precipitant, but readily soluble in  $\text{HCl}$ , forming a colorless solution. The yellow color often obtained in dissolving the hydroxide in hydrochloric acid is due to traces of ferric chloride.\*

2. **KOH** precipitates white, gelatinous beryllium hydroxide, readily soluble in an excess of the reagent, forming potassium beryllate:



The alkali beryllates are decomposed hydrolytically on boiling their dilute aqueous solutions, all of the beryllium being precipi-

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\* Haber and v. Ordt, *Zeitschr. f. anorgan. Chem.*, 38 (1904), p. 382.

† According to Hantzsch, the beryllium hydroxide is present in solution in a colloidal condition as in the case of zinc (see page 162).

tated as hydroxide. The precipitate thus obtained is, according to Haber and v. Ordt, much denser than that thrown down by ammonia, and differs from the latter by being insoluble in potassium carbonate and difficultly soluble in ammonium carbonate solutions; it is also much more difficultly soluble in dilute acids. A solution containing a considerable excess of potassium alkali hydroxide is not precipitated by boiling.

3. **Ammonium Carbonate** produces a white precipitate of beryllium carbonate, readily soluble in an excess of the reagent (difference from aluminium); by boiling the solution, the beryllium is precipitated as white basic carbonate. This property enables us to separate beryllium from iron and aluminium. The separation is not sharp, however, which can also be said of the separation by means of caustic potash.\*

4. **BaCO<sub>3</sub>** precipitates beryllium completely in the cold as hydroxide.

5. **Oxalic Acid** and **Ammonium Oxalate** cause no precipitation (difference from thorium, zirconium, erbium, yttrium, cerium, lanthanum, and didymium).

6. **K<sub>2</sub>SO<sub>4</sub>** gives with beryllium sulphate a beautifully-crystalline double salt,  $\begin{matrix} \text{SO}_4\text{—K} \\ >\text{Be} \\ \text{SO}_4\text{—K} \end{matrix} + 2\text{H}_2\text{O}$ , which is soluble in a concentrated solution of **K<sub>2</sub>SO<sub>4</sub>** (difference from Ce, La, and Di).

7. **BeCl<sub>2</sub>** is soluble in a mixture of equal volumes of saturated aqueous and ethereal hydrochloric acid, while the hydrous aluminium chloride is not (good method for separating Be and Al).†

*There are no characteristic dry reactions for beryllium.*

### ZIRCONIUM, Zr. At. Wt. 90.6.

*Occurrence.*—Zircon, **ZrO<sub>2</sub>.SiO<sub>2</sub>**, tetragonal, isomorphous with rutile, **Ti<sub>2</sub>O<sub>4</sub>**, thorite (orangite), **ThO<sub>2</sub>.SiO<sub>2</sub>**, cassiterite, **Sn<sub>2</sub>O<sub>4</sub>**, polianite, **Mn<sub>2</sub>O<sub>4</sub>**, and plattnerite, **Pb<sub>2</sub>O<sub>4</sub>**; baddeleyite, **ZrO<sub>2</sub>**, monoclinic.

Zirconium forms two oxides: Zirconium dioxide, **ZrO<sub>2</sub>**, and zirconium pentoxide, **Zr<sub>2</sub>O<sub>5</sub>**. The former is the more important

\* In order to make a quantitative separation, the beryllium hydroxide or carbonate must be redissolved and the precipitation repeated several times.

† F. S. Havens, *Z. anorg. Chem.*, **18**, 147 (1898).

and can be dissolved by heating for a long time with a mixture of two parts of concentrated  $\text{H}_2\text{SO}_4$  and one part of water and afterwards diluting. The mineral zircon,  $\text{ZrSiO}_4$ , cannot be decomposed by such treatment. It must be finely pulverized and fused with four times as much sodium carbonate at a high heat in a platinum crucible; sodium silicate,  $\text{Na}_4\text{SiO}_4$ , and sodium zirconate,  $\text{Na}_4\text{ZrO}_4$ , are formed. On treating the melt with water, the former salt dissolves, while the latter is decomposed hydrolytically, forming sodium hydroxide and sandy, insoluble zirconium hydroxide; the latter retains some of the caustic soda very persistently. After washing the residue, it is heated without previous drying with concentrated sulphuric acid at a temperature just near boiling-point, and in this way the anhydrous sulphate  $\text{Zr}(\text{SO}_4)_2$  is obtained. By pouring water over the latter the salt  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  is formed, which dissolves slowly in cold water, but more readily in hot water, forming a solution with an acid reaction.

#### REACTIONS IN THE WET WAY.

A solution of zirconium nitrate or a freshly-prepared one of zirconium oxychloride may be used for the following reactions:

1.  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  produce a white gelatinous precipitate of  $\text{Zr}(\text{OH})_4$ , insoluble in an excess of reagent.

2.  $\text{KOH}$  and  $\text{NaOH}$  likewise produce the same precipitate insoluble in an excess of reagent (difference from Al and Be). When the zirconium hydroxide is produced in the cold it is readily soluble in dilute acids; but when thrown down from a boiling solution it is very difficultly soluble in dilute acids, though it will dissolve even then in concentrated acids without difficulty.

3.  $(\text{NH}_4)_2\text{CO}_3$  produces a white, flocculent precipitate of basic carbonate, readily soluble in an excess of the reagent, but reprecipitated by boiling.

4.  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  produce white precipitates somewhat soluble in an excess, but reprecipitated by ammonia.

5.  $\text{BaCO}_3$  causes incomplete precipitation, even on boiling.

6. **Oxalic Acid** gives a white, flocculent precipitate of zirconium oxalate, readily soluble in an excess of oxalic acid, difficultly soluble in dilute hydrochloric acid, and readily soluble in ammonium oxalate. From the solution in  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  the zirconium is not precipitated by the addition of dilute  $\text{HCl}$  (difference from Th).



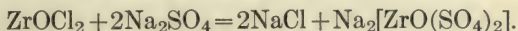
7. **Ammonium Oxalate** behaves the same as oxalic acid.

From the solution in ammonium oxalate zirconium is not precipitated on the addition of hydrochloric acid (difference from thorium).

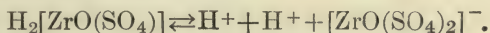
*Remark.*—A solution of zirconium sulphate behaves quite differently from that of the nitrate and oxychloride towards oxalic acid and ammonium oxalate, a fact which, although published by Berzelius and also by Pfaff, had been entirely forgotten by most chemists until their attention was recently called to it by R. Ruer.\*

On treating an aqueous solution of zirconium sulphate with oxalic acid or ammonium oxalate there is no precipitation; in fact, precipitation will not take place from nitrate or chloride solutions when these contain sufficient sulphuric acid, sodium or ammonium sulphate.

The cause of this different behavior lies in the fact that zirconium forms complex compounds with sulphuric acid and alkali sulphates. Thus the solution of zirconium sulphate contains the acid  $\text{H}_2[\text{ZrO}(\text{SO}_4)_2]$ , and on treating a solution of the oxychloride or nitrate with sodium or ammonium sulphate (but not the potassium salt) the sodium or ammonium salt of this complex acid is formed:



These compounds, however, are electrolytically dissociated in aqueous solution as follows:



As the zirconium is present in the anion it cannot react with oxalic acid.

8. **HF** causes no precipitation (difference from Th and Y).

9. **K<sub>2</sub>SO<sub>4</sub>**.—A concentrated, cold solution of  $\text{K}_2\text{SO}_4$  precipitates little by little all of the zirconium as zirconium potassium sulphate, insoluble in an excess of the reagent (difference from Al and Be). The precipitate, when produced in the cold, dissolves readily in considerable dilute HCl. If it is produced from a boiling solution, basic zirconium sulphate is formed by hydrolysis, which is quite insoluble in dilute HCl (difference from Th and Ce).

10. **Na<sub>2</sub>SO<sub>4</sub>** produces no precipitation, even on boiling the solution, which is slightly acid with sulphuric acid (difference from Ti).

---

\* Z. anorg. Chem. 42, 85 (1904).

11.  $\text{H}_2\text{O}_2$  precipitates from slightly-acid solutions white, voluminous zirconium peroxide,  $\text{Zr}_2\text{O}_5$ , which evolves chlorine on being warmed with concentrated  $\text{HCl}$ .

12.  $\text{Na}_2\text{S}_2\text{O}_3$  precipitates zirconium completely as the hydroxide, the precipitate being always contaminated with sulphur.

13. **Turmeric Paper**, after being moistened with the hydrochloric acid solution of a zirconium salt and dried, is colored reddish-brown (difference from  $\text{Th}$ ).

14.  **$\text{HCl}$** . Ruer\* recommends the following reaction for the identification of zirconium. Zirconium is precipitated in the cold by ammonia, filtered, washed, and separated from the filter as completely as possible. It is dissolved in hydrochloric acid (or if the precipitate is small in amount the paper and precipitate are treated together with not-too-strong  $\text{HCl}$  and filtered). The hydrochloric acid solution is evaporated to dryness on the water-bath and the residue taken up in a little water. To the cold, saturated solution hydrochloric acid is added drop by drop, when the presence of zirconium will be evident by the formation of a voluminous precipitate of zirconium oxychloride. The precipitate is redissolved by heating the solution, and the liquid is allowed to cool. After some time fine, silky needles of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  will precipitate.

In the somewhat unusual case that zirconium is present in the form of the insoluble meta-zirconium acid, the latter is transformed into zirconium sulphate by heating with concentrated sulphuric acid (2:1), this is dissolved in water, the zirconium precipitated by ammonia, and the above process carried out.

#### REACTIONS IN THE DRY WAY.

$\text{ZrO}_2$  is infusible in the oxyhydrogen flame (difference from the other earths), but glows brightly.

#### THORIUM, $\text{Th}$ . At. Wt. 232.4.

*Occurrence*.—Thorite (orangite),  $\text{ThSiO}_4$ , with 50–58 per cent.  $\text{ThO}_2$ ; thorianite, a mineral recently discovered in Ceylon, with 72–76 per cent.  $\text{ThO}_2$  and 11–12 per cent.  $\text{UO}_2$ ; † gadolinite,  $\text{SiO}_4\text{Be}(\text{Y}, \text{Ce}, \text{La}, \text{Di}, \text{Th}, \text{O})_2\text{Fe}$ ; monazite,  $\text{PO}_4(\text{Ce}, \text{La}, \text{Di}, \text{Th})$ , with

\* *Z. anorg. Chem.*, **42**, 85 (1904).

† *Chem.-Ztg. Rep.*, 1905, p. 91.

2-8 per cent.  $\text{ThO}_2$ ; and in the rare niobates, samarskite, pyrochlore, euxenite,\* etc. Thorite, monazite, and gadolinite are decomposed by acids, preferably sulphuric acid.

#### REACTIONS IN THE WET WAY.

A solution of  $\text{Th}(\text{SO}_4)_2$  should be used.

1.  $(\text{NH}_4)\text{OH}$ ,  $(\text{NH}_4)_2\text{S}$ , or  $\text{KOH}$  produces a white precipitate of  $\text{Th}(\text{OH})_4$ , insoluble in an excess of the reagent, but readily soluble in dilute acids. By igniting the hydroxide,  $\text{ThO}_2$  is obtained, which is only soluble in concentrated sulphuric acid after long digestion.

2.  $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  precipitates the white carbonate, soluble in an excess of the reagent, and is not reprecipitated by the addition of ammonia. On boiling, the solution becomes turbid, but clears again on cooling.

3.  $(\text{NH}_2)\text{CO}_3$  precipitates the white carbonate, readily soluble in an excess; on warming to  $50^\circ$  a basic carbonate is precipitated, which redissolves on cooling the solution. Ammonia causes no precipitation in this solution.

4.  $\text{BaCO}_3$  completely precipitates thorium salts in the cold.

5.  $\text{K}_2\text{SO}_4$  precipitates  $\text{Th}(\text{SO}_4)_4 \cdot \text{K}_4 + 2\text{H}_2\text{O}$ , difficultly soluble in water and insoluble in concentrated  $\text{K}_2\text{SO}_4$  solution (difference from Y). The corresponding sodium compound is readily soluble in water.

6. **Oxalic Acid** precipitates, from solutions which are not too acid, all of the thorium as white, crystalline oxalate, practically insoluble in oxalic and dilute mineral acids.

7. **Ammonium Oxalate** likewise precipitates thorium oxalate, which dissolves on boiling with a large excess of this reagent. The solution remains clear after cooling, provided the original solution did not contain too much free sulphuric acid, and enough ammonium oxalate was used. From the boiling solution of the ammonium double oxalate,  $\text{HCl}$  precipitates practically all of the thorium as oxalate (difference from Zr).

In the presence of ammonium acetate, ammonium oxalate produces no precipitation; but by the addition of  $\text{HCl}$  almost all of the thorium will be precipitated as oxalate.

8. **HF** produces a white, gelatinous precipitate, which soon changes to a heavy powder. **KF** causes the same reaction.

---

\* Euxenite is essentially a titanate and niobite of  $\text{Ce}(\text{La}, \text{Di})$  in which  $\text{UO}_2$  and  $\text{FeO}$  appear.



9.  $\text{Na}_2\text{S}_2\text{O}_3$  precipitates all of the thorium on boiling.  
*There are no characteristic dry reactions.*

### THE GADOLINITE METALS.

**YTTRIUM**, Y (At. Wt. 89.0), and **ERBIUM**,\* Er (At. Wt. 167.7).

*Occurrence.*—Yttrium is an important constituent of gadolinite,  $\text{SiO}_4\text{Be}(\text{Y}, \text{Ce}, \text{La}, \text{Di}, \text{Th}, \text{Er}, \text{O})_2\text{Fe}$ , and of yttrotantalite,  $(\text{Nb}, \text{Ta})\text{O}_4\text{Y}$ , an isomorphous mixture of yttrium tantalate and yttrium niobate. The two elements Y and Er are also found in cerite, thorite, and monazite.

#### REACTIONS IN THE WET WAY.

A solution of  $\text{Y}(\text{NO}_3)_3$  and one of  $\text{Er}(\text{NO}_3)_3$  should be used.

##### Yttrium.

1.  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  precipitate the white hydroxide, insoluble in an excess.

2.  $\text{KOH}$  and  $\text{NaOH}$  precipitate the white hydroxide, insoluble in an excess; the presence of tartaric acid does not prevent precipitation; but in this case yttrium tartrate is precipitated (difference from Al, Be, Th, and Zr). On igniting the precipitate, the oxide is obtained, which is readily soluble in acids.

3.  $(\text{NH}_4)_2\text{CO}_3$  produces a white precipitate of the carbonate, readily soluble in an excess of the reagent; after standing some time the solution becomes turbid, owing to the deposition of a double salt,  $\text{Y}_2(\text{CO}_3)_3 \cdot 2(\text{NH}_4)_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ .

##### Erbium.

Behaves like yttrium.

Behaves like yttrium.

Behaves like yttrium, except that the solution does not become turbid on standing.

---

\* Erbium is not an element itself, but consists of at least three elements—holmium, thulium, and dysprosium. The separation of these elements is exceedingly difficult; so we will consider simply the reactions of the mixture.

**Yttrium.**

4.  $K_2CO_3$  and  $Na_2CO_3$  precipitate the white carbonate, readily soluble in excess; after standing some time an insoluble double salt separates out.

5.  $BaCO_3$  does not precipitate yttrium in the cold, and only incompletely on warming.

6. **Oxalic acid** precipitates white yttrium oxalate, insoluble in an excess, difficultly soluble in HCl, and perceptibly soluble in ammonium oxalate.

7.  $K_2SO_4$  forms a double salt which is soluble in  $K_2SO_4$  solution (difference from Zr, Th, Ce, La, and Di).

8. **HF** produces white amorphous  $YF_3$ , which becomes pulverulent on warming, and is insoluble in water and in HF (difference from Al, Be, Ur and Ti).

Yttrium solutions do not give an absorption spectrum.

**Erbium.**

Behaves like yttrium, only the solution does not become turbid on standing.

Erbium is not precipitated at all, even on warming.

In erbium solutions, oxalic acid produces a light-red, pulverulent precipitate; otherwise the reaction is the same as with yttrium.

Behaves like yttrium.

Erbium solutions give a characteristic absorption spectrum:

$\mu\mu$	$\mu\mu$	$\mu\mu$	$\mu\mu$
683.9	640.5	<b>523.2</b>	468.5
667.1	548.9	491.6	<b>449.9</b>
653.5	541.0	<b>487.5</b>	442.3
649.0	536.4	474.5	416.6

**REACTIONS IN THE DRY WAY.**

Yttrium oxide is strongly luminous on being heated; otherwise there is no reaction.

Erbium oxide, on being heated on a platinum wire, colors the flame distinctly green. If the light is viewed through a spectroscope, a number of bright lines will be seen in the dark green which coincide with the dark lines obtained in the absorption spectrum.

## THE CERITE METALS.

CERIUM, Ce. At. Wt. 140.25. LANTHANUM, La. At. Wt. 138.9.

DIDYMIUM  $\left\{ \begin{array}{l} \text{PRASEODYMIUM, Pr. At. Wt. 140.5.} \\ \text{NEODYMIUM, Nd. At. Wt. 143.6.} \end{array} \right.$

*Occurrence.*—These three metals are important constituents of cerite,  $\text{H}_3(\text{Ca,Fe})(\text{Ce})_3\cdot\text{Si}_3\text{O}_{13}$ , and of orthite (allanite),  $(\text{AlOH}\cdot\text{Ca}_2(\text{Al,Fe,Ce})_2(\text{SiO}_4))$ , besides being usually found associated with the gadolinite earths in gadolinite, etc.

## CERIUM.

Cerium forms two oxides,  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$ ; both are basic anhydrides, from which salts are derived. The cerous salts are white, while the ceric salts are orange red.

## REACTIONS IN THE WET WAY.

## 1. Cerous Salts.

A solution of cerous nitrate,  $\text{Ce}(\text{NO}_3)_3$ , should be used.

1.  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  each produce a white precipitate of  $\text{Ce}(\text{OH})_3$ , insoluble in an excess of the reagent, but readily soluble in acids. In the presence of tartaric and citric acids, etc., the above reagents cause no precipitation (difference from Y).

2.  $\text{NaOH}$  or  $\text{KOH}$  also precipitate white  $\text{Ce}(\text{OH})_3$ , even in the presence of tartaric acid, etc. The white  $\text{Ce}(\text{OH})_3$  becomes yellow gradually on standing in the air, on account of being oxidized to  $\text{Ce}(\text{OH})_4$ .

3.  $\text{K}_2\text{CO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  each produce a white precipitate insoluble in an excess of the reagent.

4. **Oxalic Acid** or **Ammonium Oxalate** precipitate white cerous oxalate, insoluble in an excess of the reagent, and in dilute mineral acids. On ignition, white, insoluble  $\text{CeO}_2$  is formed.† If the oxalate is contaminated with praseodymium oxalate, a cinnamon-

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\* Only when the cerous oxalate is pure. If it contains traces of praseodymium, the  $\text{CeO}_2$  is obtained as a bright-yellow powder.



colored oxide is obtained, which is perfectly soluble in dilute acids.

5.  $\text{BaCO}_3$  slowly precipitates all of the cerium in the cold.

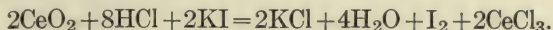
6.  $\text{K}_2\text{SO}_4$  produces a white, crystalline precipitate of the double salt  $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ , difficultly soluble in cold water, but readily soluble in hot water. It is insoluble in a saturated solution of  $\text{K}_2\text{SO}_4$  (difference from Y and Er).

## 2. Ceric Salts.

A solution of either ceric nitrate,  $\text{Ce}(\text{NO}_3)_4$ , or of ceric ammonium nitrate,  $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$ , should be used.

The beautiful orange-red color of these solutions is characteristic of all ceric salts, as is also their tendency to form difficultly soluble basic salts.

*Preparation of Ceric Compounds.*—As has been already stated, cerous hydroxide on standing in the air gradually changes to yellow, on account of the formation of ceric hydroxide. This oxidation takes place immediately on the addition of chlorine or hypochlorites. If the solution of a cerous salt is treated with caustic potash solution and chlorine is conducted into it, the white cerous hydroxide which was at first formed is quickly changed to light-yellow ceric hydroxide. The latter compound dissolves in dilute acids, forming orange solutions. It dissolves in concentrated hydrochloric acid with evolution of chlorine, forming *cerous* chloride. If white cerous hydroxide is heated in the air, it loses water and is changed into  $\text{CeO}_2$ , which is nearly white when cold, dark orange when hot, and is almost entirely insoluble in concentrated hydrochloric and nitric acids. In the presence of reducing substances (such as KI,  $\text{FeSO}_4$ , etc.) it dissolves in acids, forming cerous salts:



$\text{CeO}_2$  also dissolves in concentrated sulphuric acid with evolution of oxygen and formation of cerous sulphate. It can also be readily brought into solution by fusing with potassium pyrosulphate and dissolving the melt in considerable hot water to which a little acid is added.

If a mixture of cerous and praseodymium hydroxides is ignited in the air, a cinnamon-colored mass is obtained, which contains all

of the cerium as dioxide and is readily soluble in dilute acids, forming ceric salts. If concentrated HCl is used, there is an evolution of chlorine, the ceric salt being reduced to cerous chloride. Concentrated nitric acid dissolves it, forming cerous and ceric salts; a distinct evolution of oxygen can always be detected.

The reason why the brown mass containing a little praseodymium dissolves although the pure oxide does not, is probably the following:  $\text{CeO}_2$ , like  $\text{MnO}_2$  and  $\text{PbO}_2$  (see pages 135 and 184), plays the part of an acid anhydride, so that the brown mass contains the praseodymium as the salt of ceric acid. On treating this salt with a stronger acid, the praseodymium salt of the latter is formed, setting free ceric acid (ceric hydroxide), which in the hydrated form is readily soluble in acids, forming ceric salts.

Cerous salts can be oxidized in acid solutions by

(a) Heating with  $\text{PbO}_2$  and  $\text{HNO}_3$  (1 part of acid to 2 parts of water).

(b) Treatment with persulphuric acid.

(c) Electrolysis.

If a cerous salt is treated with hydrogen peroxide in acid solution a yellow coloration is at first formed, which soon disappears with evolution of hydrogen. Ceric salts, therefore, are *reduced* by hydrogen peroxide.

If, however, a cerous salt is treated with  $\text{H}_2\text{O}_2$  and the solution is made barely alkaline with ammonia, a dark-orange precipitate is formed which looks something like ferric hydroxide, and probably consists of  $\text{CeO}_3 + \text{H}_2\text{O}$ . This is the most sensitive reaction for cerium and is especially suited for detecting the presence of cerium in solutions of lanthanum and didymium salts.

**Basic Ceric Salts.**—If a solution of ceric nitrate is evaporated on the water-bath to a consistency of syrup, the mass dissolves readily in water after it has become cold, and the solution can be boiled without becoming turbid. If, however, a little nitric acid is added, a yellow precipitate is immediately formed, consisting of basic ceric nitrate; on the addition of more acid the precipitate redissolves. This can be explained as follows: By treating the solution of ceric nitrate with considerable water it becomes hydrolyzed considerably, but the basic salt produced is present in the *hydrosol* state and is changed by the acid into the *hydrogel* form.

As lanthanum and didymium salts do not yield basic salts under

these conditions, this property can be used for separating cerium from these metals.

It is characteristic of cerium to form with ammonium nitrate an easily crystallizable salt, ceric ammonium nitrate:



All ceric salts may be readily reduced by the ordinary reducing agents (alcohol, HI,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HNO}_2$ ,  $\text{H}_2\text{O}_2$ , etc.) to cerous salts.

#### REACTIONS IN THE DRY WAY.

The borax bead is colored dark brown when hot and light yellow to colorless when cold, after being heated in the oxidizing flame. In the reducing flame the bead becomes colorless, although strongly ignited  $\text{CeO}_2$  will remain suspended in the bead, giving it a turbid yellowish appearance.

#### LANTHANUM, La. At. Wt. 138.9.

Lanthanum forms only one oxide,\*  $\text{La}_2\text{O}_3$ , which, even after being strongly ignited, dissolves readily in acids. Its salts are colorless and yield no absorption spectrum, so that lanthanum may be distinguished in this way from didymium and erbium.

#### REACTIONS IN THE WET WAY.

A solution of lanthanum nitrate  $\text{La}(\text{NO}_3)_3$  should be used.

1.  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{S}$  precipitate a white basic salt which is difficult to filter.

2.  $\text{KOH}$  and  $\text{NaOH}$  precipitate the white hydroxide  $\text{La}(\text{OH})_3$ . There is no change to be noticed on treating with oxidizing agents (difference from Ce).  $\text{La}(\text{OH})_3$  is soluble enough in water to turn red litmus-paper blue, and it decomposes ammonium salts on warming with evolution of ammonia. The fused oxide is readily soluble in acids.

3.  $(\text{NH}_4)_2\text{CO}_3$  produces a white precipitate, insoluble in an excess of the reagent.

4. **Oxalic Acid** produces a white crystalline precipitate, insoluble in dilute mineral acids and in ammonium oxalate solution.

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\*  $\text{H}_2\text{O}_2$  is said to cause the formation of  $\text{La}_2\text{O}_5$ . Cf. Z. anorg. Chem., 21, 70 (1899).



## SUMMARY OF THE REACTIONS OF THE RARE EARTHS.

	KOH or NaOH	NH <sub>4</sub> OH or (NH <sub>4</sub> ) <sub>2</sub> S	K <sub>2</sub> CO <sub>3</sub> or Na <sub>2</sub> CO <sub>3</sub> *	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
Al <sub>2</sub> O <sub>3</sub>	White precipitate soluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate insoluble in excess.	White precipitate insoluble in excess.	White precipitate on boiling the almost neutral solution.
BeO	White precipitate soluble in excess, reprecipitated on boiling or diluting. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate very difficultly soluble in a large excess.	White precipitate readily soluble in excess and reprecipitated on boiling.†	No precipitate.
ZrO <sub>2</sub>	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess.	White precipitate slightly soluble in excess, but reprecipitated by NH <sub>4</sub> OH.	White precipitate soluble in large excess, but reprecipitated on boiling.	White precipitate (mixed with sulphur) on boiling.
ThO <sub>2</sub>	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate insoluble in excess. It is precipitated before the cerite metals.	White precipitate soluble in excess, and not reprecipitated by addition of NH <sub>4</sub> OH. The solution becomes turbid on boiling, but clears on cooling.	Behaves as with K <sub>2</sub> CO <sub>3</sub> .	Almost completely precipitated on boiling.
Y <sub>2</sub> O <sub>3</sub>	White precipitate insoluble in excess. Tartaric acid does not prevent the precipitation, but yttrium tartrate is then formed.	White precipitate insoluble in excess.	White precipitate soluble in excess. After some hours an insoluble double salt is formed.	Behaves as with K <sub>2</sub> CO <sub>3</sub> .	No precipitate.

$\text{Er}_2\text{O}_3$	Pink precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Pink precipitate insoluble in excess. Tartaric acid prevents the precipitation.	White precipitate soluble in excess. On boiling, all of the erbium is reprecipitated.	Behaves as with $\text{K}_2\text{CO}_3$ , except that the precipitate is more soluble in an excess.	No precipitate.
$\text{Ce}_2\text{O}_3$	White precipitate insoluble in excess, which is gradually colored yellow on standing in the air. Tartaric acid prevents the precipitation.	Behaves as with KOH. The precipitate becomes orange when treated with $\text{H}_2\text{O}_2$ .	White precipitate slightly soluble in excess.	Behaves as with $\text{K}_2\text{CO}_3$ .	No precipitate.
$\text{CeO}_2$	Yellow $\text{Ce}(\text{OH})_4$ is precipitated, soluble in HCl with evolution of Cl and formation of cerous chloride. After ignition it becomes insoluble in acids.	Behaves as with KOH.	Yellow precipitate almost entirely insoluble in excess.	Yellow precipitate soluble in considerable excess, but reprecipitated on boiling.	No precipitate.
$\text{La}_2\text{O}_3$	White precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Behaves as with KOH. The precipitate produced from an acetic acid solution with dilute ammonia is a basic salt, which becomes blue on treatment with iodine.	White precipitate insoluble in excess.	Behaves as with $\text{K}_2\text{CO}_3$ .	No precipitate.
$\text{Di}_2\text{O}_3$	Violet precipitate insoluble in excess. Tartaric acid prevents the precipitation.	Behaves as with KOH.	Violet precipitate of didymium carbonate, insoluble in excess.	Behaves as with $\text{K}_2\text{CO}_3$ .	No precipitate.

\* Use a double-normal solution: concentrated solutions give precipitates, in nearly every case, soluble in excess of the reagent.

† This reaction is used to separate aluminium from beryllium; the separation is not quantitative.

## SUMMARY OF THE REACTIONS OF THE RARE EARTHS.—(Continued.)

	Oxalic Acid	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	HF	$\text{BaCO}_3$	Absorption Spectrum	$\text{K}_2\text{SO}_4$
$\text{Al}_2\text{O}_3$	No precipitate.	No precipitate.	No precipitate.	Completely precipitated in the cold.	None.	No precipitate.
BeO	No precipitate.	No precipitate.	No precipitate.	Completely precipitated in the cold.	None.	No precipitate.
$\text{ZrO}_2$	White voluminous precipitate soluble in excess, difficultly soluble in very dilute HCl.	White precipitate soluble in excess, and not reprecipitated by addition of considerable HCl.	No precipitate.	No precipitate in the cold. Incompletely precipitated on warming.	None.	A concentrated solution of $\text{K}_2\text{SO}_4$ slowly precipitates zincium potassium sulphate, soluble in considerable dilute HCl unless it was precipitated from a boiling solution, when it is almost insoluble in HCl.
$\text{ThO}_2$	White precipitate insoluble in excess and in dilute mineral acids; soluble in ammonium acetate.	White precipitate soluble in excess on boiling, and not reprecipitated on cooling provided that the original solution did not contain too much free acid. The solution is precipitated by considerable HCl.	No precipitate.	Completely precipitated in the cold.	None.	Precipitates a double salt insoluble in a concentrated $\text{K}_2\text{SO}_4$ solution.
$\text{Y}_2\text{O}_3$	White precipitate insoluble in excess, and difficultly soluble in dilute HCl.	White precipitate soluble in a large excess.	White, amorphous precipitate insoluble in HF, and insoluble in dilute mineral acids after being ignited.	No precipitation in the cold. Incompletely precipitated on warming.	None.	No precipitation. The double salt is soluble in $\text{K}_2\text{SO}_4$ solution.



$\text{Er}_2\text{O}_3$	Pink precipitate insoluble in excess, difficultly soluble in dilute $\text{HCl}$ .	Pink precipitate on boiling, scarcely soluble at all.	No precipitation.	No precipitation in the cold, incompletely precipitated on warming.	Characteristic.	No precipitation; the double salt is soluble in $\text{K}_2\text{SO}_4$ solution.
$\text{Ce}_2\text{O}_3$	White precipitate insoluble in oxalic acids and in dilute mineral acids.	White precipitate insoluble in excess.	No precipitation.	Slowly but completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in $\text{K}_2\text{SO}_4$ solution.
$\text{CeO}_2$	Brown ceric oxalate is at first precipitated, which on the addition of more oxalic acid is changed to white cerous oxalate with loss of $\text{CO}_2$ .	Behaves as with oxalic acid.	No precipitation.	Completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in $\text{K}_2\text{SO}_4$ solution.
$\text{La}_2\text{O}_3$	White precipitate insoluble in excess.	Same as with oxalic acid. The precipitate is insoluble in $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .	No precipitation.	Completely precipitated in the cold.	None.	A double salt is precipitated, insoluble in $\text{K}_2\text{SO}_4$ solution.
$\text{Di}_2\text{O}_3$	Violet precipitate insoluble in excess. The solid salt shows in reflected light the well-known absorption spectrum.	Behaves as with oxalic acid.	No precipitation.	Completely precipitated in the cold.	Characteristic.	A double salt is precipitated, insoluble in $\text{K}_2\text{SO}_4$ solution.

NOTE.—These tables were compiled with the help of those published by C. Glaser, *Chem.-Zeitung*, 1896, page 612.

## ANALYSIS OF GADOLINITE (CERITE).

Gadolinite contains  $\text{SiO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{Di}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{BaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and often some of the metals of the  $\text{H}_2\text{S}$  group.

About 2 gms. of the finely-divided mineral are treated repeatedly with conc.  $\text{HCl}$ , with the addition of a little  $\text{HNO}_3$ , and evaporated to dryness on the water-bath; the mineral is completely decomposed by this treatment. The dry mass is moistened with 2 c.c. of conc.  $\text{HCl}$  (the acid is allowed to act upon the mass for fifteen minutes), 100 c.c. of water are added, and the silicic acid filtered off. The metals will be found in the filtrate, which is now saturated with  $\text{H}_2\text{S}$ , and any metals of the  $\text{H}_2\text{S}$  group filtered off. This precipitate is examined according to Table IX, page 436. The filtrate is freed from  $\text{H}_2\text{S}$  by boiling and then treated with a boiling solution of oxalic acid, added little by little, while the solution is constantly stirred. The precipitate is filtered off.

## PRECIPITATE (Ce, La, Di, Y, and Er as oxalates).

The precipitate is washed with water, dried, and ignited in a porcelain dish, whereby a cinnamon-colored mass, consisting of a mixture of the oxides of the rare metals, is obtained. It is dissolved in as little  $\text{HNO}_3$  as possible, a little alcohol is added (to reduce ceric salt to cerous), evaporated on the water-bath to dryness, dissolved in a little water, treated with an excess of solid  $\text{K}_2\text{SO}_4$ , and allowed to stand over night. In the morning the precipitate is filtered and washed with  $\text{K}_2\text{SO}_4$  solution.

PRECIPITATE (Ce, La, and Di as  $\text{R}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ )

The precipitate is dissolved in very dilute  $\text{HCl}$ , precipitated with oxalic acid, washed, dried, and ignited. The oxides formed are then dissolved in a little  $\text{HCl}$ , carefully precipitated with  $\text{NaOH}$  (avoiding an excess) and the solution is then saturated with chlorine and filtered.

## SOLUTION (Be, Al, Fe, Ca, Mg, and Na).

$\text{NH}_4\text{OH} + (\text{NH}_4)_2\text{S}$  are added and the filtrate tested in the usual way for Mg and Na. The precipitate (consisting of  $\text{Be}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{FeS}$ , and  $\text{CaC}_2\text{O}_4$ ) is filtered off, washed, dried, gently ignited, and then digested with conc.  $\text{HCl}$  and 1 c.c.  $\text{HNO}_3$  on the water-bath until completely dissolved. The excess of acid is evaporated off, the residue dissolved in water, ammonia is added, and the precipitate is filtered off. Only calcium now remains in the filtrate, which is precipitated as carbonate and confirmed as usual.

The precipitate (consisting of  $\text{Be}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_3$ ) is dissolved in a little  $\text{HCl}$ , evaporated almost to dryness, and then treated with an excess of  $(\text{NH}_4)_2\text{CO}_3$  solution, allowed to stand 15 minutes, and filtered. In case a precipitate of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  is obtained, the filtrate is treated with a few

SOLUTION (Y and Er as  $\text{R}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$ ).

The solution is precipitated with oxalic acid, filtered, ignited, and the oxides dissolved in a very little  $\text{HNO}_3$ , evaporated to dry-

drops of  $(\text{NH}_4)_2\text{S}$  (to remove the last traces of iron) until no further precipitation of  $\text{FeS}$  is formed. This is filtered off, and the filtrate is boiled for some time and filtered.

SOLUTION.

PRECIPITATE.

Rejected.

Basic beryllium carbonate.

It is dissolved in  $\text{HCl}$ , an excess of  $\text{KOH}$  is added, whereby the precipitate at first formed redissolves.

The solution is diluted with water and boiled. A white precipitate shows the presence of *Be*.

ness, dissolved in water and the solution examined with the spectroscope; black absorption bands show the presence of *Er*.

The solution is treated with  $\text{HF}$ , and the formation of a white, amorphous precipitate insoluble in  $\text{HF}$  shows the presence of *Y*.

SOLUTION ( $\text{LaCl}_3 + \text{DiCl}_3$ ).

It is acidified with  $\text{HCl}$ , boiled, precipitated with oxalic acid, filtered, washed, dried, and ignited. The oxides are dissolved in as little  $\text{HNO}_3$  as possible and examined in the spectroscope. The presence of *Di* is shown by the formation of dark absorption bands.

To test for *La*, the solution is treated with ammonium acetate, precipitated with very dilute ammonia, filtered through asbestos, and washed three times with  $\text{H}_2\text{O}$ . The precipitate is then treated with solid iodine, and if *La* is present a blue color will be noticed in a few minutes.

PRECIPITATE ( $\text{Ce}(\text{OH})_4$ ).

After being washed, the precipitate is dissolved in  $\text{HNO}_3$ , and the yellowish-orange solution is treated with  $\text{H}_2\text{O}_2$ , until decolorized, when a little dilute ammonia is added. A brown precipitate shows the presence of *Ce*.

\* Iron and aluminium are tested for in the usual way.



5.  $K_2SO_4$  precipitates white, crystalline  $La_2(SO_4)_3 \cdot 3K_2SO_4$ , insoluble in a concentrated  $K_2SO_4$  solution.

6. **Lanthanum Sulphate** is only soluble in ice-cold water; on warming the saturated solution to  $30^\circ$  the salt separates out thickly (difference from cerium).

7. **Iodine**.—If ammonia is added to a cold, dilute acetic acid solution of a lanthanum salt, and the slimy precipitate is washed with water and then treated with solid iodine, the whole mass gradually assumes a blue color which is similar to that produced by the action of iodine upon starch (this property is peculiar to lanthanum). The blue color is destroyed by the addition of acids or alkalis.

DIDYMIUM	{	NEODYMIUM, Nd. At. Wt. 143.6.
		PRASEODYMIUM, Pr. At. Wt. 140.5.

It is very difficult to separate these two metals from one another. It is accomplished only by repeated fractional crystallization of the ammonium double nitrate.

Neodymium apparently forms only one oxide,  $Nd_2O_3$ ; it appears bluish after being ignited, and is readily soluble in acids, forming violet salts, which afford a characteristic absorption spectrum.

Praseodymium, on the other hand, forms a greenish-white oxide,  $Pr_2O_3$ , which on being ignited is changed into dark-brown peroxide,  $Pr_4O_7$ . On being heated in a stream of hydrogen, the latter is reduced back to  $Pr_2O_3$ . The peroxide dissolves in acids with loss of oxygen, forming greenish salts corresponding to the lower oxide and yielding a characteristic absorption spectrum.

The **Didymium** Reactions take place with a mixture of the two elements. A solution of didymium nitrate,  $Di(NO_3)_3$ , is used.

Didymium salts are violet and show a characteristic absorption spectrum (difference from Ce and La). The behavior toward  $NH_4OH$ ,  $(NH_4)_2S$ ,  $KOH$ ,  $(NH_4)_2CO_3$ , and  $K_2SO_4$  is exactly the same as with lanthanum. Oxalic acid precipitates the reddish oxalate, which in other respects is like lanthanum oxalate.

**TANTALUM**, Ta. (At. Wt. 181), and **NIOBIUM**, Nb (At. Wt. 94).

These two rare elements, belonging to the nitrogen-vanadium group, form oxides of the formula  $R_2O_5$ , which behave as acid anhydrides and should have been considered, perhaps, under the acids. Since, however, tantalic and niobic acids are soluble,

under certain conditions, in strong acids and from these solutions are precipitated by ammonia and ammonium sulphide, it seems better to consider them at this place.

*Occurrence.*—In the form of meta-acids these elements appear in the isomorphous minerals tantalite,  $\text{Fe}(\text{TaO}_3)_2$  and niobite or columbite,  $\text{Fe}(\text{NbO}_3)_2$ . In tantalite a part of the tantalic acid is replaced by niobic acid and a part of the iron by manganese. Niobite shows an analogous behavior.

In the form of pyroacids the two elements occur as an isomorphous mixture in the mineral yttrotantalite,  $\text{Y}_4(\text{Ta}_2\text{O}_7)_3$  and  $\text{Y}_4(\text{Nb}_2\text{O}_7)_3$ . Finally tantalum, and to some extent niobium, replaces the phosphorus in monazite;  $(\text{Ce}, \text{La}, \text{Di})\text{PO}_4$ . Tin is usually found in all the above minerals and often tungsten; conversely cassiterite and wolframite often contain small quantities of niobic and tantalic acids.

#### TANTALUM, Ta. At. Wt. 181.

Metallic tantalum\* is ductile, although the presence of a little impurity makes it harder than tool steel. Its specific gravity is 16.5 and melting-point  $2250^\circ \text{C}$ . On ignition in the air it assumes a yellow to blue tinge caused by a thin coating of oxide. Tantalum is not attacked by boiling  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , or even aqua regia, but it is slowly dissolved by hydrofluoric acid with evolution of hydrogen; any metal remaining undissolved is then brittle on account of absorbed hydrogen. The concentrated solution in hydrofluoric acid forms with concentrated  $\text{KOH}$  insoluble, crystalline potassium tantalum fluoride,  $\text{K}_2(\text{TaF}_7)$ . By evaporating the solution in  $\text{HF}$  with concentrated  $\text{H}_2\text{SO}_4$  until the former acid is all expelled, the residue dissolves in a little cold water, but the solution becomes turbid on dilution or especially by boiling.

Tantalum forms two oxides,  $\text{Ta}_2\text{O}_4$  and  $\text{Ta}_2\text{O}_5$ , the former being indifferent chemically and the latter an acid anhydride. After ignition the pentoxide is insoluble in acid and is not rendered soluble by fusion with pyrosulphate, although it is volatilized by heating with ammonium fluoride. Fusion of the oxide with

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\* W. von Bolton, Z. Electrochemie, 11 (1905), Heft 6, p. 45.

caustic alkali in a silver crucible gives rise to alkali tantalates, both the meta- and hexatantalates being known; only the former are soluble in water.

Potassium hexatantalate,  $K_8Ta_6O_{19} + 16H_2O$ , is soluble in water and caustic potash solution, while the sodium salt is soluble in water, but not in caustic soda. The remaining tantalates are all insoluble.

#### REACTIONS IN THE WET WAY.

A solution of potassium hexatantalate should be used.

1. **Mineral Acids.**—(a)  $H_2SO_4$  precipitates tantalic acid from cold dilute solutions, and the precipitation becomes almost quantitative only on boiling. Hot concentrated  $H_2SO_4$  dissolves the precipitate produced by the dilute acid. On diluting the solution with water after it has become cold, the tantalic acid is reprecipitated (difference from niobium).

(b) **HCl** at first produces a precipitate from a concentrated solution, which dissolves in an excess of the acid, forming an opalescent solution. From this solution sulphuric acid precipitates tantalic acid in the cold, but the precipitation is not quantitative even on boiling.

(c)  **$HNO_3$**  has the same action as **HCl**.

2.  **$NH_4OH$**  and  **$(NH_4)_2S$**  precipitate from the hydrochloric acid solution either tantalic acid itself or an acid ammonium tantalate; tartaric acid prevents the precipitation.

3. **Tannic Acid** produces in acid solutions a light-brown precipitate (difference from niobic acid).

4.  **$K_4[Fe(CN)_6]$**  produces in acid solutions a light-yellow precipitate, which becomes brown on the addition of a little ammonia.

5.  **$H[KF_2]$** .—If a concentrated solution of tantalic acid in hydrofluoric acid is treated with **KF**, the difficultly-soluble  **$K_2[TaF_7]$**  is formed, which separates from the solution in the form of orthorhombic needles (200 parts of water dissolve 1 part of salt) (difference from niobium). On boiling the solution of tantalic potassium fluoride, the very difficultly-soluble oxyfluoride precipitates ( **$K_4Ta_4O_5F_{14}$** ). By means of this reaction the merest trace of tantalic acid can be detected in the presence of niobic acid.

6. **Zn** and **HCl** do not produce colored solutions (difference from niobium).



REACTIONS IN THE DRY WAY.

$Ta_2O_5$  is infusible. The bead of salt of phosphorus remains colorless in both oxidizing and reducing flames. The addition of  $FeSO_4$  does not cause the formation of a blood-red color (difference from Ti and Nb).

NIOBIUM.

Sp. Gr. = 12.7. M. Pt. = 1950° C.

The metal niobium shows great similarity to tantalum; it is more readily attacked by acids.

Niobium forms three oxides:  $Nb_2O_2$ ,  $Nb_2O_4$ , and  $Nb_2O_5$ , of which the last is an acid anhydride.  $Nb_2O_5$ , like  $Ta_2O_5$ , is insoluble in acids after it has been ignited and is not rendered soluble by fusing with potassium pyrosulphate. The melt dissolves in cold water, but niobic acid separates from the solution on boiling. By fusing with KOH or  $K_2CO_3$ , potassium hexaniobate,  $K_8Nb_6O_{19} \cdot 16H_2O$ , is formed, which is soluble in water. The corresponding sodium salt is insoluble in caustic soda, but soluble in water.

REACTIONS IN THE WET WAY.

A solution of potassium hexaniobate should be used.

1. **Mineral Acids** produce in alkali niobate solutions a white, amorphous precipitate of niobic acid, which is only slightly soluble in an excess of the acid. Concentrated sulphuric acid, however, dissolves the niobic acid on warming, and the solution remains clear after being diluted with cold water (difference from tantalum).

If the niobic acid is treated with boiling hydrochloric acid, it only dissolves slightly, but on pouring off the acid, the residue is soluble in water.†

2.  $NH_4OH$  and  $(NH_4)_2S$  precipitate niobic acid from the sulphuric acid solution, and the precipitate is soluble in HF.

3. **Tannic Acid Tincture** produces an orange-red precipitate.

4.  $K_4[Fe(CN)_6]$  produces a light-yellow precipitate.

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\* Werner von Bolton, Chem. Zentralbl., 1905, I, 586.

† This behavior reminds one of metastannic acid. (Cf. p. 250.)

5.  $\text{H}[\text{KF}_2]$ .—If niobic acid is dissolved in an excess of  $\text{HF}$  and  $\text{KF}$  is then added, readily soluble niobic potassium fluoride is formed (12.5 parts of water dissolve 1 part of the salt). By boiling the dilute aqueous solution, soluble potassium niobic oxyfluoride is formed, which is even more soluble (difference from tantalum).

6. **Zinc** produces a beautiful blue coloration when added to an acid solution of niobic acid (difference from tantalum).

#### REACTIONS IN THE DRY WAY.

The bead of salt of phosphorus is blue, violet, or brown in the reducing flame (according to the amount of niobic acid which is present) the bead becomes red on the addition of  $\text{FeSO}_4$ .

### METALS OF THE $\text{H}_2\text{S}$ GROUP.

THALLIUM, VANADIUM, MOLYBDENUM, TUNGSTEN, SELENIUM, TELLURIUM, RHODIUM, PALLADIUM, OSMIUM, IRIDIUM, RUTHENIUM.

#### THALLIUM, $\text{Tl}$ . At. Wt. 204.0.

*Occurrence.*—Thallium is found in nature very sparingly; in small amount in many varieties of pyrite, and accompanying potassium in carnallite and sylvite, in many lithium micas and in many mineral waters. It replaces the silver to a considerable extent in copper-silver selenide, in crookesite,  $(\text{AgTlCu})_2\text{Se}$ , and in berzelianite,  $(\text{CuAgTl})_2\text{Se}$ . There are no characteristic thallium minerals. The principal sources of our thallium is the dust from sulphuric acid plants where pyrite containing thallium is used.

Metallic thallium reminds one of lead in its color, softness, high specific gravity, and low melting-point.

	Lead.	Thallium.
Specific gravity.....	11.25 to 11.39	11.8
Melting-point.....	327.1° C.	301.7° C.

Thallium dissolves readily in nitric and sulphuric acids, but not in hydrochloric acid. It forms two oxides: thallos oxide,  $\text{Tl}_2\text{O}$ , and thallic oxide,  $\text{Tl}_2\text{O}_3$ ; both are anhydrides of bases and from them thallos and thallic salts are derived.

## REACTIONS IN THE WET WAY.

## A. Thallous Compounds.

Thallous compounds are colorless and soluble in water as a rule. The sulphide, chloride, bromide, iodide, and chromate are insoluble in water. Thallous oxide is a colorless powder, whose aqueous solution reacts alkaline and absorbs carbon dioxide with avidity.

A solution of thallous sulphate should be used for the following reactions:

1.  $\text{H}_2\text{S}$  causes no precipitation from solutions which contain mineral acids; in neutral solutions, thallium is incompletely precipitated as black thallous sulphide,  $\text{Tl}_2\text{S}$ .  $\text{Tl}_2\text{S}$  is readily soluble in mineral acids, but insoluble in acetic acid and alkaline sulphides. It is oxidized readily on standing in the air to thallous sulphate.

2.  $(\text{NH}_4)_2\text{S}$  precipitates all of the thallium as  $\text{Tl}_2\text{S}$ .

3.  $\text{KOH}$ ,  $\text{NaOH}$ , or  $\text{NH}_4\text{OH}$  produces no precipitation.

4. **Alkali Carbonates** cause precipitation only in very concentrated solutions, for thallous carbonate is fairly soluble (100 parts of water dissolve 5 parts of the salt).

5.  $\text{HCl}$  produces a heavy, white precipitate of thallous chloride, very slightly soluble in water, and still less so in water containing a little hydrochloric acid.

6.  $\text{KI}$  precipitates yellow thallous iodide,  $\text{TlI}$ , from even the most dilute solutions; this is the most sensitive reaction for thallium.

7. **Alkali Chromates** precipitate yellow thallous chromate, insoluble in cold nitric or sulphuric acids.

8.  $\text{H}_2[\text{PtCl}_6]$  precipitates light-yellow thallium chloroplatinate, which is almost entirely insoluble in water; 1 part dissolves in 15,585 parts of water at  $15^\circ\text{C}$ . and in 1948 parts of water at  $100^\circ\text{C}$ .

9.  $\text{Al}_2(\text{SO}_4)_3$ .—If a solution of thallous sulphate is treated with aluminium sulphate and the solution is then allowed to crystallize, glistening, colorless octahedrons are obtained of thallium alum,  $\text{TlAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ .

Thallium is like lead in respect to its specific gravity and to the solubility of its halogen compounds; but, on the other hand, it is similar to the alkalies with regard to the solubility and alkaline reaction of the hydroxide and carbonate, and with regard to its forming an insoluble chloroplatinate and an alum.



### B. Thallic Compounds.

Thallic compounds cannot as a rule be prepared by the oxidation of thallic compounds (with the exception of thallic chloride, which is readily obtained by the action of chlorine water upon thallic chloride). They are obtained by the solution of thallic oxide\* in acids, and can be distinguished from thallic compounds by the ease with which they suffer decomposition in aqueous solution. Thus thallic sulphate is decomposed on boiling its aqueous solution into thallic hydroxide and sulphuric acid; the nitrate behaves similarly.

The chloride,  $\text{TlCl}_3$ , is a hygroscopic and not very stable substance; on being heated to  $100^\circ \text{C}$ . chlorine is evolved with the formation of thallic chloride.

$\text{KOH}$ ,  $\text{NaOH}$ , and  $\text{NH}_4\text{OH}$  precipitate brown thallic hydroxide,  $\text{Tl}(\text{OH})_3$ , from solutions of thallic salts, which changes to  $\text{TlO}(\text{OH})$  on standing in the air, is difficultly soluble in acids and insoluble in an excess of alkali.

$\text{KCl}$  and **alkali chromates** do not cause precipitation.

$\text{KI}$  precipitates thallic iodide with deposition of iodine.

#### REACTIONS IN THE DRY WAY.

Thallium salts color the non-luminous gas-flame a beautiful emerald green. The thallium spectrum consists of a green line.

### VANADIUM, V. At. Wt. 51.0.

*Occurrence.*—Vanadinite,  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ ; carnotite; † mottramite,  $(\text{CuPb})_2\text{V}_2\text{O}_{10} + 2\text{H}_2\text{O}$ ; many clays and in almost all granites.

Vanadium, like nitrogen, forms five oxides:  $\text{V}_2\text{O}$ ,  $\text{V}_2\text{O}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{V}_2\text{O}_4$ ,  $\text{V}_2\text{O}_5$ .

The first three of these oxides are basic anhydrides. Compounds representing these valencies of vanadium are not en-

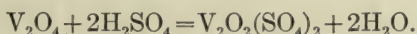
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\*  $\text{Tl}_2\text{O}_3$  is not attacked in the cold by concentrated sulphuric acid, but is dissolved on warming. The hydrated oxide,  $\text{TlO}(\text{OH})$ , is much more soluble.

† According to Friedel and Cumenge, carnotite contains 18 per cent.  $\text{V}_2\text{O}_5$  and 55 per cent.  $\text{VO}_3$ , as well as K, Ca, Ba, H, As, and P. (Cf. Hillebrand and Ransome, *Am. J. Science*, 10, 138.)

countered in qualitative analysis except, to some extent, in the tests for vanadium with strong reducing agents. The oxides  $V_2O_4$  and  $V_2O_5$  represent the types of vanadium compounds usually encountered in analytical chemistry.

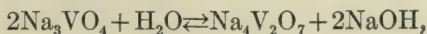
$V_2O_4$  is the anhydride of hypovanadic acid,  $V_2O_2(OH)_4$ . This compound is an amphoteric substance and forms salts with both acids and bases.  $V_2O_4$  itself is a blue powder, soluble in concentrated acids, forming blue divanadyl salts.



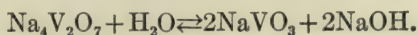
If the solution of divanadyl sulphate is treated with sodium carbonate or ammonia (avoiding excess), hypovanadic acid separates out as a grayish-white precipitate, which, like the anhydride, is soluble in acids with blue color and in alkalis with a brown color. The alkali hypovanadates correspond to the symbols  $Na_2V_2O_6$  and  $Na_2V_4O_{10}$ . Hypovanadates of other metals are for the most part insoluble in water and such precipitates may form when an acid solution containing vanadium is neutralized. The divanadyl compounds are readily formed by reducing solutions of the pentoxide in mineral acids with sulphurous acid (cf. page 488), and serve, on account of their blue color, for the detection of vanadium.

$V_2O_5$  is the anhydride of vanadic acid and is an orange-red crystalline mass, which is readily fusible but non-volatile. It is only slightly soluble in water, forming a slightly-acid, yellow solution, but readily soluble in concentrated solutions of caustic alkalis, forming vanadates.

Like phosphoric acid, vanadic acid exists in the form of meta-, pyro-, ortho-, and poly-compounds, of which the meta-compounds are the most stable and the ortho-compounds the least so. Thus an aqueous solution of potassium or sodium orthovanadate is hydrolyzed, even in the cold, into the pyro-salt and alkali hydroxide,



and on boiling the meta-salt is formed:



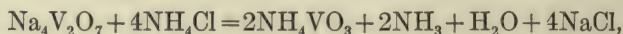
The meta-, pyro-, and ortho-salts of the alkalis are colorless or slightly yellow, while the polyvanadates, *e.g.*, the tetra- and hexavanadates, are intensely orange or reddish. Thus the colorless or light-yellow solutions of the ortho-, meta-, and pyrovanadates are colored intensely orange on the addition of acid.

Besides the above types of vanadium compounds, this element is known as pervanadic acid,  $\text{HVO}_4$ , formed by the addition of hydrogen peroxide to the acid solution of a vanadate.

The reactions of quadrivalent and quinquevalent vanadium will be considered together; the other forms are not common enough to make it necessary to describe their characteristic reactions.

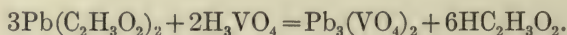
#### REACTIONS IN THE WET WAY.

1.  $\text{NH}_4\text{Cl}$ .—If a piece of solid ammonium chloride is added to a solution of an alkali vanadate, colorless ammonium metavanadate separates out,



difficultly soluble in a concentrated solution of ammonium chloride.

2.  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  precipitates vanadic acid quantitatively as yellow lead vanadate:



This precipitate, however, is more soluble in dilute nitric acid than is lead chromate, and it is possible to separate chromic acid from vanadic acid by treating the solution of the two acids with lead nitrate in dilute nitric acid solution; under the proper conditions all but a fraction of a milligram of the chromium is precipitated and 100 mgms. of vanadium yield no precipitate.\* The vanadium can be detected in the filtrate by the  $\text{H}_2\text{O}_2$  test.

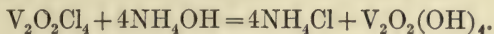
3.  $\text{NH}_4\text{OH}$  added to a solution of an alkali vanadate causes no precipitation. Vanadic acid behaves like phosphoric acid toward ammonia; vanadates of ferric iron, aluminium and uranium are likely to be precipitated by ammonia, as well as vanadates of the alkaline earth metals.

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\* The solution is neutralized exactly with  $\text{NaOH}$ , 2 c.c. of  $\text{HNO}_3$  (sp. gr. 1.20) are added and an excess of 20 per cent.  $\text{Pb}(\text{NO}_3)_2$  solution.



$\text{NH}_4\text{OH}$  added to a solution of a vanadyl salt precipitates dark gray hypovanadic acid:



The precipitation is not quantitative and small quantities of vanadium may remain in solution when the vanadyl salt is alone present. If, however, an excess of ferric chloride is added to the solution, the vanadium is quantitatively precipitated upon the addition of ammonia. This is true both with vanadic acid and with vanadyl salt, ferric vanadate and ferric hypovanadate being precipitated with the ferric hydroxide. Instead of ferric chloride, an aluminium or uranium salt may be used for the same purpose.

4.  $(\text{NH}_4)_2\text{S}$  produces no precipitation, but causes the solution to turn brown, owing to the formation of sulpho-salts. If hydrogen sulphide is conducted into a strongly ammoniacal solution of a vanadate or hypovanadate, the solution at first turns yellowish-red, but the color slowly deepens until eventually a characteristic, brilliant, violet-red color is obtained when the solution has become saturated with  $\text{H}_2\text{S}$ . Ammonium salts interfere somewhat with this test, but their influence is overcome by the addition of a large excess of ammonia. The red color is probably caused by the formation of ammonium sulphovanadate. As little as 0.2 mgm. of vanadium can be recognized by the red color.

The addition of acid to the red solution produces a black precipitate of  $\text{V}_2\text{S}_4$  or  $\text{V}_2\text{S}_5$ .\* The precipitate is soluble in alkalies, alkali carbonates, and in alkali sulphides, forming a brown solution.

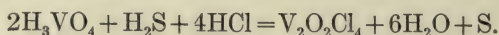
Molybdenum gives a similar red color, in case it was not completely removed by previous treatment with hydrogen sulphide in acid solution, and obscures the above test or may be mistaken for vanadium.

5.  $\text{H}_2\text{S}$  gives no precipitation in acid solution, but reduces

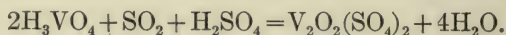
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\* The precipitation is not quantitative; the filtrate is always colored blue and contains detectable amounts of vanadyl salts.

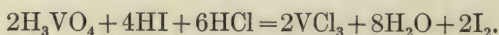
compounds of vanadic acid to divanadyl compounds, so that the solution is colored blue:



**6. Reducing Agents** ( $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HBr}$ , alcohol, oxalic and tartaric acids, sugar, etc.) reduce acid solutions containing vanadates to blue vanadyl salts:



$\text{HI}$  reduces vanadic acid to green salt of  $\text{V}_2\text{O}_3$ :



The green color only appears after the iodine has been removed by continued boiling of the solution.

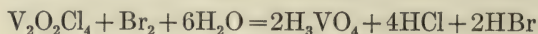
Metals, such as  $\text{Zn}$ ,  $\text{Al}$ , and  $\text{Cd}$ , cause still further reduction of vanadic acid, so that the solution turns at first blue, then green, and finally violet.

Boiling an acid solution of a vanadate with concentrated hydrochloric acid and alcohol reduces the vanadium quantitatively to divanadyl salt. Treatment of vanadic acid with ferrous salt also reduces the former to divanadyl salt and the excess of the ferrous iron can be oxidized by cold potassium dichromate solution without oxidizing the vanadium.

**7.  $\text{H}_2\text{O}_2$ .**—If an acid solution of a vanadate is treated with a few drops of  $\text{H}_2\text{O}_2$  and shaken, the solution becomes colored reddish brown owing to the formation of pervanadic acid,  $\text{HVO}_4$ , insoluble in ether. This is a very delicate reaction.

**8. Mercurous Nitrate** precipitates white mercurous vanadate from neutral solutions of a vanadate; the precipitate is soluble in nitric acid.

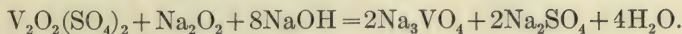
**9. Oxidizing Agents** convert divanadyl compounds into vanadic acid. The oxidation may be effected by bromine in hydrochloric acid solution:



by dilute potassium permanganate in hot, very dilute sulphuric acid solution:



or by sodium peroxide in alkaline solution:



Chromium, aluminium, vanadium and uranium may be separated from iron, nickel, cobalt and manganese by means of this reaction; the chromate is left in solution as sodium chromate,  $\text{Na}_2\text{CrO}_4$ , the aluminium as sodium aluminate,  $\text{NaAlO}_2$ , the vanadium as sodium vanadate,  $\text{Na}_3\text{VO}_4$ , the uranium as sodium peruranate, and the zinc as sodium zincate,  $\text{Na}_2\text{ZnO}_2$ ; while the iron is precipitated as  $\text{Fe}(\text{OH})_3$ , the nickel as  $\text{Ni}(\text{OH})_2$  or  $\text{Ni}(\text{OH})_3$ , the cobalt as  $\text{Co}(\text{OH})_3$ , and the manganese as hydrated  $\text{MnO}_2$ .

#### Detection of Vanadium in Rocks (Hillebrand).\*

Five gms. of the finely-powdered rock are fused over the blast-lamp with 20 gms. of  $\text{Na}_2\text{CO}_3$  and 3 gms. of  $\text{NaNO}_3$ . The product of the fusion is extracted with water, the manganate formed is reduced by the addition of a little alcohol, and the solution is filtered. The aqueous solution can contain As, P, Mo, Cr, V, W. It is nearly neutralized with nitric acid (the amount necessary having been determined by a blank test), almost evaporated to dryness, taken up in water, and filtered. The alkaline solution is then treated with mercurous nitrate, whereby mercurous phosphate, arseniate, chromate, molybdate, and tungstate with some basic mercurous carbonate are precipitated. The solution is boiled and filtered, the precipitate dried and separated from the filter, ignited in a platinum crucible, and then fused with a little sodium carbonate. The product of the fusion is extracted with water, when a yellow color shows that chromium is present. The solution is acidified with sulphuric acid, and traces of Pt, Mo, and As are precipitated by means of  $\text{H}_2\text{S}$  (best in a small suction flask). This precipitate is filtered off and the excess of  $\text{H}_2\text{S}$  is removed from the filtrate by boiling, while a stream of carbonic acid gas is being passed through it; the solution is evaporated to dryness, and the excess of sulphuric acid removed by carefully heating in an air-bath. The residue is now dissolved in 2 or 3 c.c. of water and shaken with a few drops of  $\text{H}_2\text{O}_2$ ; a brownish-yellow color shows the presence of vanadium. If chromium is present, on adding  $\text{H}_2\text{O}_2$  and ether to the sulphuric acid solution and shaking, the ether will be colored blue by chromium and the aqueous solution yellow by vanadium.†

\* Amer. J. of Science, 1898, p. 209.

† E. Champagne, Chem. Zentralbl., 1904, II, p. 1167.

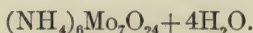


## REACTIONS IN THE DRY WAY.

The borax bead is colorless in the oxidizing flame if slightly saturated with the vanadium compound, yellow if strongly saturated, and green in the reducing flame.

**MOLYBDENUM, Mo. At. Wt. 96.0.**

*Occurrence.*—Molybdenite,  $\text{MoS}_2$ ; wulfenite,  $\text{PbMoO}_4$ ; powellite,  $\text{CaMoO}_4$ . Molybdenum has a valence of 2, 3, 4, and 6, and forms the following oxides:  $\text{MoO}$ ,  $\text{Mo}_2\text{O}_3$ ,  $\text{MoO}_2$ , and  $\text{MoO}_3$ . The first three are basic anhydrides, while the last oxide,  $\text{MoO}_3$ , is an acid anhydride, forming a white mass (yellow when warm) which is readily fusible, but very difficultly volatile. In the cooler part of the crucible, colorless, transparent, thin, orthorhombic plates of  $\text{MoO}_3$  are deposited.  $\text{MoO}_3$  is only very slightly soluble in water, but dissolves readily in alkalis and in ammonia, forming molybdates. Molybdic acid itself can be readily obtained as a solid mass by acidifying the solution of an alkali molybdate; it is soluble in an excess of the acid (difference from tungstic acid). The most important commercial molybdate is the acid ammonium molybdate, corresponding to the formula



## REACTIONS IN THE WET WAY.

A solution of ammonium molybdate should be used.

The alkali molybdates are soluble in water; the remaining salts are mostly insoluble in water but soluble in acids.

1. **Dilute Acids** precipitate from concentrated alkali molybdate solutions white  $\text{H}_2\text{MoO}_4$ , soluble in an excess of acid.

**Concentrated Sulphuric Acid.**—If a trace of a molybdenum compound is evaporated with a drop of concentrated sulphuric acid almost to dryness in a porcelain dish, the mass is colored intensely blue. This is an exceedingly delicate reaction.

2.  $\text{H}_2\text{S}$  at first colors acid molybdenum solutions blue, and precipitates little by little the molybdenum as brown molybdenum trisulphide,  $\text{MoS}_3$ , soluble in ammonium sulphide, forming a brown solution from which  $\text{MoS}_3$  is reprecipitated by the addition of acids.

Molybdenum sulphide is oxidized by treatment with concentrated nitric acid, or by roasting in the air, into  $\text{MoO}_3$  or molybdic acid.

3. **Zinc.**—If a molybdate solution which is acid with hydrochloric or sulphuric acid is treated with zinc, the solution is colored at first blue, then green, and finally brown. Other reducing agents such as  $\text{SnCl}_2$ ,  $\text{Hg}_2(\text{NO}_3)_2$ , etc., cause the same reaction.

4. **KCNS** causes no change when added to acid molybdenum solutions, but if the solution is then treated with zinc or stannous chloride, a blood-red coloration is produced on account of the formation of molybdenum sulphocyanide; the reaction also takes place in the presence of phosphoric acid (difference from iron). If the solution is shaken with ether, the colored compound is dissolved in the latter.

5. **Sodium Phosphate.**—If a few drops of a solution of sodium phosphate are added to a molybdate solution strongly acid with nitric acid, a yellow crystalline precipitate of ammonium phosphomolybdate is formed, slowly in the cold, but much more quickly on warming the solution (cf. Phosphoric Acid, page 366). Arsenic acid causes the precipitation of a similar compound (cf. p. 217).

6. **Mercurous Nitrate** precipitates white mercurous molybdate from neutral solutions; the precipitate is soluble in nitric acid.

8. **Lead Acetate** precipitates white lead molybdate, soluble in nitric acid.

8. **Potassium Ferrocyanide** produces a reddish brown precipitate. A very sensitive test.

#### REACTIONS IN THE DRY WAY.

Alkali molybdates, alone or with sodium carbonate, are reduced on charcoal to gray molybdenum, a white incrustation of  $\text{MoO}_3$  being formed at the same time.

**Salt of Phosphorus Bead.** All molybdenum compounds color the bead, but the color depends upon the concentration. In the oxidizing flame the hot bead is colored brownish yellow to yellow; it becomes yellowish-green on cooling and finally colorless. In the reducing flame the bead becomes dark brown when hot and grass green when cold. The borax bead\* is similar but not quite as characteristic.

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\* O. Lutz, Z. anal. Chem., 1908, 1.

### Separation of Molybdenum, Arsenic, Antimony, and Tin.

These elements are all precipitated as sulphides upon the introduction of hydrogen sulphide into an acid solution. They are separated from the members of the copper group by treatment with ammonium polysulphide solution, in which their sulphides are soluble. On acidifying this solution of the sulphosalts with dilute hydrochloric acid, the molybdenum, arsenic, antimony and tin are reprecipitated as sulphides. This precipitate is filtered off, washed, dried and introduced, little by little, into a nickel crucible containing a molten mixture of 10 parts  $\text{Na}_2\text{O}_2$ , and 10 parts  $\text{Na}_2\text{CO}_3$  for each part of sulphide precipitate. The contents of the crucible, after all the sulphide has been introduced, are fused for ten minutes over the Bunsen burner, then cooled and extracted with cold water. The aqueous solution thus obtained may contain sodium arseniate and sodium molybdate and the insoluble residue may consist of sodium antimonate and tin dioxide. The residue is removed by filtration and washed with a normal solution of sodium hydroxide. The filtrate is tested for arsenic by making it strongly ammoniacal and adding magnesium mixture. A white crystalline precipitate of magnesium ammonium arseniate is formed if arsenic is present, but only after standing for some time with a little arsenic. The filtrate from the magnesium ammonium arseniate precipitate is saturated with hydrogen sulphide to convert any molybdenum present into ammonium sulphomolybdate; and the solution is then acidified with dilute hydrochloric acid. The precipitated sulphide is filtered off, treated with concentrated nitric acid in a porcelain crucible and tested for molybdenum with concentrated sulphuric acid, as described on page 490.

*Test for Antimony and Tin.* The residue insoluble in dilute caustic soda solution is treated with a mixture of equal parts concentrated hydrochloric acid and water, the solution placed in contact with a piece of platinum foil and tested for antimony and tin as described in Table IX, page 436.



**TUNGSTEN, W.** At. Wt. 184.

M. Pt. = 3,000°.

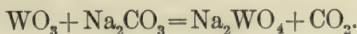
*Occurrence.*—Tungsten is not very often found in nature, but there are a number of well-crystallizing tungsten minerals, such as the minerals of the Scheelite group.

Scheelite,  $\text{CaWO}_4$ ; cuproscheelite,  $(\text{CaCu})\text{WO}_4$ ; reinite,  $\text{FeWO}_4$ ; stolzite,  $\text{PbWO}_4$ . These minerals all crystallize in the tetragonal system and form with powellite,  $\text{CaMoO}_4$ , and wulfenite,  $\text{PbMoO}_4$ , a very interesting isomorphous group. Another isomorphous group, which consists of minerals crystallizing in the monoclinic system, is formed by hübnerite,  $\text{MnWO}_4$ ; wolframite,  $(\text{MnFe})\text{WO}_4$ , and ferberite,  $\text{FeWO}_4$ . The most important tungsten mineral is wolframite, which is usually contaminated with small amounts of silicic, tantalic, and niobic acids. Tungsten forms two oxides,  $\text{WO}_2$  and  $\text{WO}_3$ .

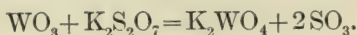
$\text{WO}_2$  is a brown powder, readily obtained by heating  $\text{WO}_3$  to dull redness in a stream of hydrogen. It is pyrophoric and must, therefore, be cooled in a stream of hydrogen before it is allowed to come into contact with the air. By igniting strongly in a stream of hydrogen, metallic tungsten is obtained, which is stable in the air. This behavior is important and is taken advantage of in the quantitative determination of tungsten.

$\text{WO}_3$  is an acid anhydride obtained by the ignition of tungstic acid, of ammonium or mercurous tungstates, or by the oxidation of the dioxide, on heating in the air.

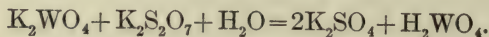
The trioxide is a canary-yellow powder, insoluble in water and dilute acids, and only slightly soluble in concentrated hydrochloric and hydrofluoric acids. It dissolves readily by warming with potassium or sodium hydroxides, and less readily in ammonia. It is most easily dissolved by fusing with sodium carbonate, sodium tungstate being formed:



It is changed to potassium tungstate by fusing with potassium pyrosulphate:



If the product of this last fusion is treated with water, usually none of the tungsten goes into solution, because if an excess of potassium pyrosulphate is present (which is usually the case) it reacts with the potassium tungstate, forming free tungstic acid:



If not enough pyrosulphate remains to complete the above decomposition, some of the tungsten will be dissolved, but never all of it. If a little sulphuric acid is added to the water, none of the tungsten will go into solution. This property enables one to separate tungsten from titanium. If ammonium carbonate were added, all of the tungsten dissolves, which enables us to separate tungstic from silicic acid.

#### REACTIONS IN THE WET WAY.

A solution of sodium tungstate should be used.

1. **Mineral Acids**,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , produce, in the cold, a white, amorphous precipitate of hydrated tungstic acid,  $\text{H}_2\text{WO}_4 + \text{H}_2\text{O}$ .\* By boiling the solution, the yellow anhydrous acid  $\text{H}_2\text{WO}_4$  is obtained, insoluble in dilute acids, but soluble to an appreciable extent in concentrated hydrochloric acid.

Tungstic acid must always be washed with water which contains acid or a dissolved salt, as otherwise tungstic acid will form a pseudo-solution with pure water, so that a turbid filtrate will be obtained (cf. pages 90, 199).

Phosphoric acid behaves differently toward solutions of the alkali tungstates than do the other mineral acids; it produces a white precipitate soluble in an excess of phosphoric acid; a complex phospho-tungstic acid is formed, *e.g.*,  $\text{OP}(\text{WO}_3)_{12}(\text{ONa})_3$ . If the solution of an alkali tungstate is boiled with free tungstic acid, the latter gradually goes into solution, forming a metatungstate;



Mineral acids cause no precipitation in solutions of metatungstates. If the solution is boiled with an excess of acid, the soluble metatungstic acid is gradually changed to insoluble, ordinary tungstic acid, which is then precipitated.

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\* The presence of tartaric acid prevents the precipitation.

2.  $\text{H}_2\text{S}$  produces no precipitation in acid solutions.

3.  $(\text{NH}_4)_2\text{S}$  gives no precipitation in a solution of an alkali tungstate, but if the solution is afterward acidified, light-brown tungsten trisulphide is precipitated, which has the property of forming pseudo-solutions with pure water, but is insoluble in hydrochloric acid. The precipitate redissolves in ammonium sulphide.

4. **Reducing Agents.**—If the solution of an alkali tungstate is treated with  $\text{HCl}$  and zinc, the tungstic acid at first precipitated by the  $\text{HCl}$  is soon turned to a beautiful blue color, owing to the formation of  $\text{W}_2\text{O}_5$ .

$\text{SnCl}_2$  produces a yellow coloration at first, but on adding  $\text{HCl}$  and warming, a beautiful blue precipitate is obtained. This is one of the most sensitive reactions for tungstic acid.

5. **Mercurous Nitrate** precipitates white mercurous tungstate from neutral solutions.

6. **Lead Acetate** precipitates white lead tungstate from neutral solutions.

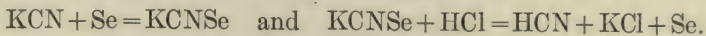
#### REACTIONS IN THE DRY WAY.

The salt of phosphorus bead is colorless in the oxidizing flame, and blue in the reducing flame, becoming blood red on the addition of a little  $\text{FeSO}_4$ .

**SELENIUM, Se.** At. Wt. 79.2.

Sp. Gr. = 4.28–4.5. M. Pt. =  $200^\circ \text{C}$ .

*Occurrence.*—Although selenium is quite widely distributed in nature, it is invariably found in very small amounts, usually replacing sulphur, forming isomorphous compounds with lead, silver, copper, and mercury; clausthalite,  $\text{PbSe}$ ; berzelianite,  $(\text{CuAgTl})_2\text{Se}$ ; naumannite,  $(\text{Ag}_2, \text{Pb})\text{Se}$ ; tiemannite,  $\text{HgSe}$ ; lehrbachite,  $(\text{Pb}, \text{Hg})\text{Se}$ ; onofrite,  $\text{Hg}(\text{SeS})$ ; eucairite,  $(\text{Ag}, \text{Cu})_2\text{Se}$ . It is also found in small amounts in many varieties of pyrite and chalcopyrite, and indeed the small amounts which are found in these minerals form the chief source of the selenium of commerce. By roasting these minerals (as in the manufacture of sulphuric acid) all of the selenium is volatilized, and is consequently deposited in the lead chambers as a mud from which it is extracted with a solution of potassium cyanide and afterwards precipitated with acid:



Selenium, like sulphur, exists in two allotropic forms. The modification soluble in carbon disulphide is obtained by reducing



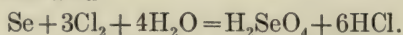
selenious acid in the cold with sulphurous acid; it is a *brick-red* powder. After heating this *red* selenium with hot water for some time it is changed into *black* selenium, and is then *insoluble* in carbon disulphide.

On heating in the air, selenium burns with a bluish flame (giving off an odor similar to that of rotten radishes) forming white crystalline selenium dioxide,  $\text{SeO}_2$ , which will sublime on being heated in a stream of oxygen. Selenium forms one oxide,  $\text{SeO}_2$ , and two acids: selenious acid,  $\text{H}_2\text{SeO}_3$ , and selenic acid,  $\text{H}_2\text{SeO}_4$ .

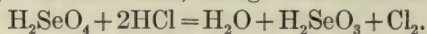
Selenious acid,  $\text{H}_2\text{SeO}_3$ , is obtained in the form of long colorless needles by oxidizing selenium with nitric acid or aqua regia,\* or by the solution of its anhydride,  $\text{SeO}_2$ , in water. Unlike sulphurous acid, it is not changed on standing in the air into selenic acid; but, on the contrary, is reduced by dust, etc., to red selenium. The acid is dibasic, and forms salts in which either one or both of the hydrogen atoms are replaced by metal.

The acid salts are all soluble in water, but the neutral salts are all insoluble with the exception of those of the alkalies.

Selenic acid,  $\text{H}_2\text{SeO}_4$ , is obtained in solution by conducting chlorine into water which contains either suspended selenium or dissolved selenious acid:



Sodium seleniate is obtained by fusing selenium with sodium carbonate and potassium nitrate. Selenic acid is a dibasic acid and behaves similarly to a peroxide, evolving chlorine when boiled with concentrated hydrochloric acid, being reduced to selenious acid:

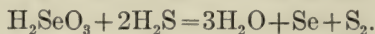


#### REACTIONS IN THE WET WAY.

##### (a) *Selenious Acid.*

A solution of either potassium selenite or of free selenious acid should be used.

1.  $\text{H}_2\text{S}$  produces a lemon-yellow precipitate, consisting of selenium and sulphur, from solutions in water or in dilute hydrochloric acid:



The precipitate is soluble in ammonium sulphide.

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\* If a solution of selenium in aqua regia is evaporated, considerable selenium is lost by volatilization; the addition of KCl or NaCl to the solution prevents such loss.

2. **Reducing Agents** ( $\text{SO}_2$ ,  $\text{SnCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{HI}$ ,  $\text{NH}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4$ ,  $\text{NH}_2\text{OH} \cdot \text{HCl}$ ) reduce the solution of selenious acid in dilute hydrochloric acid, causing the precipitation of *red* selenium, which changes black after the solution has been heated for some time.  $\text{H}_3\text{PO}_3$  precipitates selenium from hot concentrated solutions, but does not from a dilute solution slightly acid with  $\text{HCl}$ .

3.  $\text{BaCl}_2$  precipitates from neutral solutions white barium selenite,  $\text{BaSeO}_3$ , soluble in dilute acids.

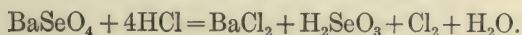
4.  $\text{CuSO}_4$  produces a greenish-blue, crystalline precipitate (difference from selenic acid).

(b) *Selenic Acid*.

A solution of potassium seleniate should be used.

1.  $\text{H}_2\text{S}$  causes no precipitation unless the solution is boiled with hydrochloric acid. In the latter case the selenic acid is reduced first to selenious acid and then to selenium by the hydrogen sulphide, which precipitates together with free sulphur.

2.  $\text{BaCl}_2$  gives a white precipitate of barium seleniate,  $\text{BaSeO}_4$ , insoluble in water and in dilute acids, soluble, with evolution of chlorine, on being boiled with hydrochloric acid:



3.  $\text{CuSO}_4$  produces no precipitation.

4.  $\text{SO}_2$  does not reduce selenic acid.

**Method for Testing Sulphuric Acid for Selenium.\***

Five or six drops of the acid to be tested are added to the solution of a little codein in sulphuric acid, when, if selenium is present, a green coloration will be apparent. The test is a very delicate one.

REACTIONS IN THE DRY WAY.

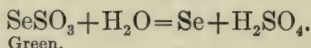
All selenium compounds emit the odor of decayed radishes on being mixed with sodium carbonate and heated on charcoal before the blowpipe.

If a selenium compound is heated at the end of a thread of asbestos in the upper reducing flame of the Bunsen burner, it will be reduced to selenium; and if a test-tube filled with water is held above

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\* Dragendorff, Chem. Zentralbl., 1900, 944.

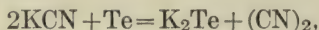
the flame, a red coating of selenium will be deposited upon the glass.\* If a few drops of concentrated sulphuric acid † are placed in a larger test-tube (large enough to hold the smaller test-tube) and the tube on which the selenium is deposited is emptied and placed within the larger tube, the selenium will dissolve ‡ in the sulphuric acid, forming a green solution; but on the addition of water, red selenium will be reprecipitated (difference from tellurium):



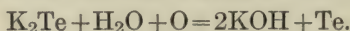
**TELLURIUM, Te.** At. Wt. 127.5.

Sp. Gr. = 6.1-6.4. M. Pt. = 450° C.

*Occurrence.*—Tellurium is a rarer metal than selenium, always occurring in the form of a telluride, and usually combined with the noble metals: calaverite, (Au,Ag)Te<sub>2</sub>; krennerite, (Au,Ag)Te<sub>2</sub>; sylvanite, (Au,Ag)Te<sub>4</sub>; nagyagite, Au<sub>2</sub>Sb<sub>2</sub>Pb<sub>10</sub>Te<sub>6</sub>S<sub>15</sub>; coloradoite, HgTe; silver telluride, Ag<sub>2</sub>Te; and often in small amounts in galena and copper ores. Emmonsite of Cripple Creek, Colorado, is a ferric telluride with 70.71 per cent. TeO<sub>2</sub> and 22.76 per cent. Fe<sub>2</sub>O<sub>3</sub>. Tellurium itself is a bluish-white, brittle substance, which melts at 450° C. and can be distilled in a stream of hydrogen. It burns in the air with a bluish-green flame, forming tellurium dioxide, TeO<sub>2</sub>. It is insoluble in carbon disulphide, and can be oxidized by means of nitric acid to tellurous acid. On being fused with potassium cyanide, out of contact with the air, it is changed to potassium telluride,



which dissolves in water, forming a cherry-red solution. If air is conducted through this solution, the tellurium is precipitated in the form of a black powder (difference from selenium):



Tellurium may be separated from selenium by means of this last reaction. The two metals are fused with potassium cyanide, the melt is treated with water, and the tellurium precipitated by passing

\* Cf. page 37.

† The sulphuric acid should be freed from water by heating in a platinum crucible to a temperature just below the boiling-point, and the crucible with its contents allowed to cool in a desiccator.

‡ Slowly in the cold, readily on warming.



a current of air through the solution; the selenium is precipitated from the filtrate by acidifying with hydrochloric acid. Tellurium forms two oxides:  $\text{TeO}_2$  and  $\text{TeO}_3$ .

Tellurium dioxide (the anhydride of tellurous acid) is usually obtained in the form of a white mass, which melts on gentle heating, forming a yellow liquid. Tellurium dioxide does not sublime (difference from selenium). It is scarcely soluble at all in water, is slightly soluble in ammonia and in dilute acids, but readily soluble in concentrated acids or in caustic potash solutions.  $\text{TeO}_2$  dissolves in fairly concentrated sulphuric acid, forming the basic sulphate,  $\text{Te}_2\text{O}_3 \cdot \text{SO}_4$ , while with nitric acid it forms the basic nitrate,  $\text{Te}_2\text{O}_3(\text{OH})\text{NO}_3$ . Both of these compounds are hydrolyzed readily, forming insoluble tellurous acid; the latter in turn loses water and forms the anhydride.

On dissolving  $\text{TeO}_2$  in caustic potash, potassium tellurite,  $\text{K}_2\text{TeO}_3$ , is obtained. *Only the alkali tellurites are soluble in water.*

Tellurium trioxide (telluric anhydride) is formed by heating telluric acid. It is a yellow powder, insoluble in water and nitric acids, scarcely affected by boiling with concentrated hydrochloric acid, but is readily dissolved by boiling with a concentrated solution of potassium hydroxide (but not by sodium hydroxide), forming potassium tellurate.

Telluric acid,  $\text{H}_2\text{TeO}_4 + 2\text{H}_2\text{O}$ , is a very weak acid, obtained by oxidizing tellurous acid with chromic acid, and precipitating the telluric acid by the addition of concentrated nitric acid. The acid forms a colorless crystalline mass, is readily soluble in water, and is converted by means of concentrated hydrochloric acid into tellurous acid, with evolution of chlorine. The acid dissolves readily in caustic potash (or soda) solution, forming the readily soluble alkali tellurate, which reacts strongly alkaline in aqueous solution.

By gently heating the hydrated telluric acid, the anhydrous acid,  $\text{H}_2\text{TeO}_4$ , is obtained in the form of a white powder and is totally different from the hydrated acid. The latter is *soluble* in water and in caustic alkalies, and is *completely reduced* by boiling with concentrated hydrochloric acid; but the anhydrous acid is *insoluble* in water and in concentrated sodium hydroxide solution, and is only very slightly attacked by boiling concentrated hydrochloric acid, although readily soluble in warm potassium hydroxide solution.

Only the tellurates of the alkalies are soluble in water; the others

are usually obtained in the form of amorphous precipitates soluble in acids.

#### REACTIONS IN THE WET WAY.

##### (a) Tellurous Acid.

A solution of potassium tellurite,  $K_2TeO_3$ , should be used.

1.  $H_2S$  precipitates from acid solutions brown  $TeS_2$ , which is readily soluble in ammonium sulphide.

2. **Reducing Agents.**— $SO_2$  precipitates tellurium completely from *dilute* hydrochloric acid solutions in the form of a black powder, even in the presence of tartaric acid; but from a strongly-acid solution no tellurium is precipitated even on boiling (difference from selenium). In the latter case about 200 c.c. of hydrochloric acid (sp. gr. 1.175) are used (cf. Vol. 2).

$SnCl_2$  or  $Zn$  causes black tellurium to precipitate from solutions which are not too acid.

$H_3PO_3$  precipitates the tellurium only from concentrated solutions, not at all from cold dilute solutions.

$FeSO_4$  reduces neither tellurous nor telluric acids (difference from selenium).

3.  $HCl$  produces a white precipitate of  $H_2TeO_3$ .

##### (b) Telluric Acid.

A solution of potassium tellurate should be used.

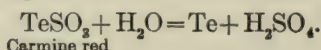
1.  $HCl$  causes no precipitation; but if the solution is boiled chlorine is evolved, and on dilution with water tellurous acid is precipitated.

2.  $H_2S$  and reducing agents have the same effect upon hot solutions of tellurates as upon tellurites.

3. **Lead Salts** precipitate difficultly-soluble lead tellurate.

#### REACTIONS IN THE DRY WAY.

Metallic tellurium is formed by heating any telluride in the upper reducing flame, and can be collected on the lower surface of a test-tube filled with water in the form of a black film, soluble in concentrated sulphuric acid. The latter solution is of a carmine-red color (difference from selenium); and on the addition of water black tellurium is deposited:



## THE PLATINUM METALS.

## PLATINUM, PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM AND IRIDIUM.

Platinum has been already described on page 264.

**PALLADIUM, Pd.** At.Wt. 106.7.

Sp. Gr. = 11.8. M. Pt. = 1549° C.

*Occurrence.*—The platinum metals form an isodimorphous group, but only in the case of palladium are both forms known—the isometric and the hexagonal:

(a) Isometric System.

Platinum (Pt, Fe).

Iridium (Ir, Pt).

Platinum iridium (Pt, Ir, Rh).

Palladium (Pd, Pt, Ir).

(b) Hexagonal System.

Iridosmium (Sysserskit) (Ir, Os).

Osmiridium (Newjanskit) (Ir, Os,  
Pt, Rh, Ru) or (Os, Ir, Rh).

Palladium (Pd, Pt, Ir).

*Properties.*—Rolled, hammered, or cast palladium possesses an almost silver-white color, but when precipitated from solutions it is in the form of a black powder. If it is suspended in water when in the finely-divided form, it is transparent with a reddish color. Palladium has the lowest melting-point of all the platinum metals, viz., 1549° C. On being heated in the air, it appears bluish, owing to the formation of  $\text{Pd}_2\text{O}$ ; the latter, however, is decomposed by stronger heating.

Behavior towards acids: Although the other platinum metals are attacked by no acid except aqua regia, palladium is dissolved slowly by warm nitric acid (also in the cold when it is alloyed with other metals such as Cu, Ag, etc.), forming a brown solution of  $\text{Pd}(\text{NO}_3)_2$ .

Finely-divided, precipitated palladium is soluble in hydrochloric acid when exposed to the action of air at the same time, and less readily soluble in sulphuric acid. It is readily attacked by fusing with potassium pyrosulphate, forming soluble palladium sulphate,  $\text{PdSO}_4$ .

The best solvent for palladium is aqua regia.

Finely-divided palladium has the very characteristic property



of being able to adsorb almost 700 times its own volume of hydrogen, and possesses consequently a very strong catalytic action. If hydrogen and oxygen (air) are conducted at the same time over some gently-ignited, finely-divided, metallic palladium, the hydrogen is burnt to water, and in the same way carbon monoxide may be changed to carbon dioxide. Methane, however, is only decomposed by igniting the palladium more strongly, so that this gives us a method for separating methane from a mixture of H and CO (cf. Vol. 2, Gas Analysis).

Palladium forms two oxides, both of which possess strongly basic properties:  $\text{PdO}$  and  $\text{PdO}_2$ . From the former the palladous, and from the latter the palladic, compounds are derived. The palladous compounds are much more stable than the palladic compounds, and the latter constantly exhibit the tendency to change into the former.

By dissolving finely-divided palladium in hydrochloric acid, palladous chloride is obtained; or, better, by dissolving the metal in aqua regia, in which case a mixture of palladous and palladic chlorides is at first obtained. If this solution, however, is evaporated to dryness, palladic chloride loses chlorine and is completely changed into palladous chloride, so that on treating the residue with water a solution of palladous chloride is obtained. Since palladic chloride is decomposed completely by evaporation, it is evident that palladic chloride cannot exist in hot solutions.

#### REACTIONS IN THE WET WAY.

##### (a) *Palladous Compounds.*

A solution of palladous chloride,  $\text{PdCl}_2$ , should be used.

1.  $\text{H}_2\text{S}$  precipitates black palladous sulphide from acid and neutral solutions. The precipitate,  $\text{PdS}$ , is insoluble in ammonium sulphide, but soluble in boiling hydrochloric acid, or more readily in aqua regia.

2.  $\text{KOH}$  or  $\text{NaOH}$  precipitates a brown basic salt, soluble in an excess of the reagent. If the solution is acidified with  $\text{HCl}$ ,  $\text{KOH}$  produces no precipitate (difference from platinum).

3.  $\text{Na}_2\text{CO}_3$  produces a brown precipitate of palladous hydroxide, soluble in excess but reprecipitated on boiling.

4.  $\text{NH}_4\text{OH}$  gives a flesh-colored precipitate of  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]_n$ \* soluble in an excess of ammonia, forming a colorless solution (containing palladodiamine chloride,  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ ), from which yellow crystalline palladosamine chloride,  $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ , is precipitated on the addition of hydrochloric acid. The latter compound is difficultly soluble in dilute hydrochloric acid and is used for the preparation of pure palladium.

In a solution of palladous nitrate, ammonia causes no precipitation, but forms colorless palladodiamine nitrate,  $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ .

5.  $\text{NH}_4\text{Cl}$  forms a soluble complex salt:  $[\text{PdCl}_4](\text{NH}_4)_2$ .

6.  $\text{KCl}$ , when added to a concentrated solution, causes the precipitation of difficultly-soluble, reddish-brown  $[\text{PdCl}_4]\text{K}_2$  (octahedrons).

7.  $\text{HI}$  or  $\text{KI}$  produces a black precipitate of palladous iodide, even in very dilute solutions. The precipitate is insoluble in water, alcohol, ether, and  $\text{HI}$ , but soluble in  $\text{KI}$  and  $\text{NH}_3$ . (This and the following reaction are characteristic for palladium.)

8.  $\text{Hg}(\text{CN})_2$  produces a yellowish-white gelatinous precipitate of palladous cyanide,  $\text{Pd}(\text{CN})_2$ , difficultly soluble in  $\text{HCl}$ , readily soluble in  $\text{KCN}$  and  $\text{NH}_3$ . On being ignited, the spongy metal remains.

9. **Reducing Agents.**— $\text{H}_2\text{SO}_3$ , formic acid ( $\text{HCOOH}$ ),  $\text{Zn}$ ,  $\text{Fe}$ ,  $\text{FeSO}_4$ ,  $\text{Cu}_2\text{Cl}_2$ ,† alcohol, and  $\text{CO}$  ‡ reduce palladium salts to the metal itself.

In the presence of  $\text{HCl}$ , stannous chloride forms at first a red, then a brown, and finally a green, solution; but in the absence of the acid,  $\text{SnCl}_2$  causes a partial reduction to the metal, while the solution turns green.

\* This compound is an isomer of palladosamine chloride, and is often written thus:  $\text{PdCl}_2, \text{Pd}(\text{NH}_3)_4\text{Cl}_2$ .

† In the presence of considerable  $\text{NaCl}$  or  $\text{HCl}$  there is no reduction with  $\text{Cu}_2\text{Cl}_2$ .

‡  $\text{PdCl}_2 + \text{CO} + \text{H}_2\text{O} = 2\text{HCl} + \text{CO}_2 + \text{Pd}$ . This reaction enables us to detect small amounts of  $\text{CO}$  in gas mixtures; *e.g.*, in the air. For this purpose the gas is led by means of a small drawn-out glass tube into 10 c.c. of a solution which contains 1 mg. of  $\text{PdCl}_2$  and 2 drops of dilute  $\text{HCl}$ . If  $\text{CO}$  is present, black  $\text{Pd}$  will be deposited, and the solution will become decolorized little by little. (Potain and Drouin, *Compt. rend.*, 126, 938.)

*(b) Palladic Compounds.*

These give the same reactions as palladous compounds, on account of their being readily changed into the latter. The principal difference, however, is the insolubility of the ammonium salt of chloropalladic acid. If a concentrated, cold solution of palladous chloride is shaken with chlorine water and then treated with ammonium chloride, a red crystalline precipitate of  $[\text{PdCl}_6](\text{NH}_4)_2$  is soon formed.

## REACTIONS IN THE DRY WAY.

All palladium compounds are decomposed on ignition, leaving behind the metal, which is soluble in nitric acid or in aqua regia, and the solution thus obtained can be tested by the above reactions.

**RHODIUM, Rh. At. Wt. 103.0.**

Sp. Gr. = 12.6. M. Pt. = 2000° C.

*Properties.*—Rhodium possesses the color and lustre of aluminium; it is more infusible than platinum, its melting-point lying at 2000° C.; on cooling the hot metal it sputters and appears bluish, owing to oxidation. The solubility of rhodium depends entirely upon the fineness of the material.

When precipitated from a solution of its chloride by means of formic acid or other reducing agents at a temperature not exceeding 100° C., it exists in an extremely finely-divided state (rhodium-black) and dissolves readily in boiling concentrated sulphuric acid, or more readily in aqua regia. If, however, the finely-divided metal is ignited strongly, it becomes (like the compact metal) almost insoluble in aqua regia.

If rhodium is alloyed with other metals (Pb, Zn, Bi, Cu, etc.), it is left in a finely-divided condition after treatment of the alloy with acids, and is consequently soluble in aqua regia. When it is alloyed with much platinum or palladium a considerable amount of rhodium will dissolve in aqua regia; but when it is alloyed with a little platinum, most of the rhodium and a part of the platinum remain undissolved.

On being fused with potassium pyrosulphate, potassium rhodium



sulphate is formed, which dissolves in water, forming a yellow solution, but becomes red on the addition of HCl.

Rhodium forms three oxides:  $\text{RhO}$ ,  $\text{Rh}_2\text{O}_3$ , and  $\text{RhO}_2$ ; all possess a well-defined basic nature. The sesquioxide,  $\text{Rh}_2\text{O}_3$ , alone \* forms a series of salts, of which sodium-rhodium chloride is the most important for the analytical chemist; for when in this form it is easiest to bring rhodium into solution. This salt is prepared by mixing the finely-divided metal very intimately with twice as much dry sodium chloride, placing it in a porcelain boat and gently igniting it in a current of moist chlorine gas. The salt thus formed has the composition  $[\text{RhCl}_6]\text{Na}_3$ , and is soluble in water (45 parts of water dissolve 1 part of the salt). From this solution large, dark-red, glistening triclinic prisms of  $[\text{RhCl}_6]\text{Na}_3 \cdot 9\text{H}_2\text{O}$  can be crystallized out.

#### REACTIONS IN THE WET WAY.

A solution of sodium rhodium chloride should be used.

1.  $\text{H}_2\text{S}$  precipitates (very slowly in the cold, but much more quickly on warming) black rhodium sulphide,  $\text{Rh}_2\text{S}_3$ ; insoluble in  $(\text{NH}_4)_2\text{S}$ , soluble in boiling nitric acid.

2.  $\text{KOH}$  and  $\text{NaOH}$  produce at first no precipitate; but after standing some time a yellow precipitate of rhodium hydroxide,  $\text{Rh}(\text{OH})_3 + \text{H}_2\text{O}$ , separates out. The precipitate is soluble in an excess of the reagent, but is reprecipitated on boiling in the form of brownish-black  $\text{Rh}(\text{OH})_3$ .

If a solution of potassium rhodium sulphate were used,  $\text{KOH}$  precipitates the yellow compound immediately.

On adding  $\text{KOH}$  to a solution of rhodium chloride, at first no precipitate is produced; but on the addition of a little alcohol brownish-black rhodium hydroxide is deposited.

3.  $\text{NH}_4\text{OH}$  produces (in concentrated solutions and after standing some time) a yellow precipitate of chloropurpureorhodium chloride,  $\text{Rh}(\text{NH}_3)_5\text{Cl}_3$ , insoluble in hydrochloric acid.

4.  $\text{KNO}_3$ , on being warmed with sodium rhodium chloride solution, causes the precipitation of difficultly-soluble, orange-yellow  $\text{Rh}(\text{NO}_2)_6\text{K}_3$ , soluble in  $\text{HCl}$ .

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\* A sodium-rhodium sulphite of the formula  $4\text{Rh}(\text{SO}_3), 6\text{Na}_2\text{SO}_3 + 9\text{H}_2\text{O}$  was prepared by Bunsen.

5. **Reducing Agents.**—Formic acid in the presence of ammonium acetate precipitates the black metal, as does zinc in the presence of acids.

#### REACTIONS IN THE DRY WAY.

All rhodium compounds are reduced to metal on being heated in a stream of hydrogen, or by heating on charcoal with sodium carbonate before the blowpipe. The metal is easily recognized by its insolubility in aqua regia, its being brought into solution by fusing with potassium pyrosulphate and then treating with water, and by the formation of the brown hydroxide when KOH and a little alcohol are added to the solution thus obtained.

#### OSMIUM, Os. At. Wt. 191.

Sp. Gr.=21.3–22.477. M. Pt.=about 2500° C.

Osmium and ruthenium are distinguished from the other platinum metals by their forming volatile oxides.

*Properties.*—The compact metal possesses a bluish-white color, very similar to zinc, and is the heaviest of all metals. It can be melted by heating in an electric furnace.\* Very finely divided osmium is oxidized by the air † at ordinary temperatures, and at about 400° C. it ignites and burns rapidly to  $\text{OsO}_4$ , which is volatile at 100° C. The denser the metal the higher the temperature necessary to effect the oxidation.

*Behavior towards Acids.*—In the compact condition osmium is insoluble in all acids; but in the finely-divided state (as obtained by treating its zinc alloy with nitric acid) it is soluble in nitric acid, more soluble in aqua regia, and most soluble in fuming nitric acid, forming osmium tetroxide; the latter can be separated from the solution by distillation.

Compact osmium is brought into solution by fusing with NaOH and either  $\text{KNO}_3$  or  $\text{KClO}_3$ . The melt contains a salt of perosmic acid ( $\text{OsO}_4$ ).

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\* F. Mylius and R. Dietz, Ber., 1898, 3187.

† Cf. Ot. Sulc, Z. anorgan. Chemie, 19, 332.

Osmium forms five oxides:

$\text{OsO}_2$ , Osmious oxide, grayish-black, insoluble in acids	$\text{Os}_2\text{O}_3$ , Osmium sesquioxide, black, insoluble in acids	$\text{OsO}_2$ , Osmic oxide, black-gray, insoluble in acids
$[\text{OsO}_3]$ , Osmic acid, known only in derivatives	$\text{OsO}_4$ , Perosmic acid, colorless needles soluble in water	

Osmium tetroxide,  $\text{OsO}_4$ , (the anhydride of perosmic acid,) is the most important osmium compound in the eyes of the analytical chemist, and is obtained by the oxidation of the substance in the air by dissolving the finely-divided metal in fuming nitric acid or in aqua regia, or by fusing with  $\text{NaOH}$  and  $\text{KNO}_3$  or  $\text{KClO}_3$ , treating the melt with nitric acid and distilling. Osmium tetroxide is a colorless, crystalline mass which sublimes at a comparatively low temperature and melts, forming colorless vapors at  $100^\circ \text{C}$ . The vapor has a chlorine-like odor, attacks the mucous membrane, and is poisonous.

The chlorides of osmium can only be obtained in the dry way;  $\text{OsCl}_2$ ,  $\text{OsCl}_3$ ,  $\text{OsCl}_4$  are known. The potassium salt of the hypothetical hydrochlorosmic acid,  $\text{H}_2\text{OsCl}_6$ , forms dark-red octahedrons, soluble in water and decomposed by boiling the solution. By heating finely-divided osmium with  $\text{KCl}$  in a current of chlorine,  $\text{K}_2[\text{OsCl}_6]$  is formed; it dissolves in cold water, forming a red solution.

#### REACTIONS IN THE WET WAY.

A solution of  $\text{K}_2[\text{OsCl}_6]$  should be used.

1. If a solution of osmium chloride is treated with dilute nitric acid, the mixture distilled from a small retort, and the vapors received in caustic soda solution, the latter will be colored yellow, owing to the formation of potassium osmiate. If this solution is now acidified, osmium tetroxide is set free, and can be recognized by its very penetrating odor. On adding a little sodium thiosulphate to the acid solution and warming, a brown precipitate of osmium sulphide is formed.

2.  $\text{H}_2\text{S}$  precipitates brownish-black osmium sulphide, insoluble in ammonium sulphide.

3.  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  or  $\text{K}_2\text{CO}_3$  precipitate reddish-brown osmium hydroxide  $\text{Os}(\text{OH})_4$ .



4. **Reducing Agents** —If the solution of the chloride is treated with tannic acid or alcohol and a little hydrochloric acid is added, it is colored dark-blue, owing to the formation of osmium dichloride,  $\text{OsCl}_2$ ; KI colors the solution a deep reddish-purple.

5. **Indigo** is decolorized by solutions containing  $\text{OsO}_4$ . Ferrous sulphate precipitates black osmium dioxide; stannous chloride produces a brown precipitate soluble in HCl, forming a brown solution.

#### REACTIONS IN THE DRY WAY.

All osmium compounds are reduced to metal on being heated in a stream of hydrogen.

#### RUTHENIUM, Ru. At. Wt. 101.7.

Sp. Gr. = 12.261, crystallized; 11.0, fused. M. Pt. = above  $1950^\circ \text{C}$ .

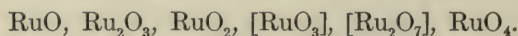
*Properties.*—Ruthenium exists in the form of a dark gray or black powder, and in the form of bright porous sticks; it is brittle, can be powdered, and is melted in the oxyhydrogen flame.

On being melted, a part of the ruthenium is oxidized to ruthenium tetroxide, a volatile substance having a penetrating odor similar to that of  $\text{OsO}_4$ . The molten metal spurts on cooling.

*Behavior towards Acids.*—Ruthenium is almost completely insoluble in all acids, even aqua regia. By fusing with KOH and  $\text{KNO}_3$  (or  $\text{KClO}_3$ ) it is oxidized to potassium ruthenate,  $\text{K}_2\text{RuO}_4$ .

On heating with NaCl in a current of chlorine, soluble  $\text{K}_2\text{RuCl}_6$  is formed. The solution in water of the greenish-black melt is of an orange-yellow color, and colors the human skin black. Ruthenium is unaffected by fusing with potassium pyrosulphate.

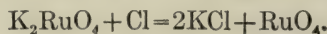
It forms the following oxides:



The most important of the oxides is  $\text{RuO}_4$ . It is formed:

(a) By roasting the metal itself, or its oxide, above  $1000^\circ \text{C}$ . (osmium formed the volatile tetroxide at  $400^\circ \text{C}$ .)

(b) By fusing the metal with KOH and  $\text{KNO}_3$  in a silver crucible, dissolving the melt in water, saturating the cold solution with chlorine gas, and distilling the solution from a small retort:



(c) By treating the solution of potassium-ruthenium chloride with KOH and Cl, and subsequently distilling.

(d) By distilling potassium-ruthenium chloride with  $\text{KClO}_3$  and HCl.

*By distilling a dilute solution after the addition of nitric acid no  $\text{RuO}_4$  will be evolved* \* (difference from osmium).

Ruthenium tetroxide forms gold-yellow, glistening orthorhombic needles that are very volatile and emit a characteristic odor; it boils at  $100^\circ \text{C}$ . and is only slightly soluble in water. It is changed by the addition of alcohol and HCl into ruthenium trichloride,  $\text{RuCl}_3$  (or sesquichloride,  $\text{Ru}_2\text{Cl}_6$ ). If the solution of the latter salt is made ammoniacal, treated with sodium thiosulphate and warmed, an intense reddish-violet coloration will be produced. (This is a very sensitive and characteristic reaction.)

On treating a solution of potassium ruthenate with nitric acid, black  $\text{Ru}(\text{OH})_3$  is precipitated; it dissolves in hydrochloric acid, forming a yellow solution of  $\text{RuCl}_3$ .

#### REACTIONS IN THE WET WAY.

A solution of  $\text{RuCl}_3$  should be used.

1.  $\text{H}_2\text{S}$  produces no precipitation at first, but after some time the solution becomes azure-blue, and brown ruthenium sulphide is precipitated (very sensitive and characteristic).

2.  $(\text{NH}_4)_2\text{S}$  precipitates the brownish-black sulphide, difficultly soluble in an excess of the reagent.

3. KOH and NaOH precipitate black ruthenium hydroxide,  $\text{Ru}(\text{OH})_3$ , soluble in acids but insoluble in alkalies.

4. KCNS, in the absence of other platinum metals, produces gradually a red, then purple, and on warming a violet, coloration (very characteristic).

5.  $\text{KNO}_2$  imparts an orange-yellow color to the solution, owing to the formation of  $\text{K}_3[\text{Ru}(\text{NO}_2)_6]$  becoming a beautiful dark red on the addition of a little colorless ammonium sulphide; on adding more ammonium sulphide, brown ruthenium sulphide is precipitated.

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\* In the presence of concentrated nitric acid, however,  $\text{RuO}_4$  is formed:



6. **Zinc** at first colors the solution of the chloride azure blue, but subsequently the solution is decolorized and ruthenium itself is precipitated.

7. **Hydroxylamine** reduces ruthenium tetrachloride to ruthenium trichloride (difference from platinum).

### IRIDIUM, Ir. At. Wt. 193.1.

Sp. Gr. = 22.4. M. Pt. = 2500° C.

*Properties.*—When produced by the ignition of iridium ammonium chloride, it is obtained in the form of a gray, spongy mass, very difficultly soluble in aqua regia. After being strongly ignited, it is almost completely insoluble in aqua regia.

It is more soluble in aqua regia when it is precipitated from solutions in a very finely-divided form by means of formic acid, or when it is alloyed with other metals (Au, Ag). The metal is unaffected by fusing with potassium pyrosulphate (difference from rhodium). It is oxidized by fusing with NaOH and KNO<sub>3</sub> in a silver crucible, but the compound formed (Ir<sub>2</sub>O<sub>3</sub> combined with sodium) is only partly soluble in water. If the melt is treated with aqua regia, however, a dark-red solution of Na<sub>2</sub>[IrCl<sub>6</sub>] will be obtained.

By heating the metal with NaCl in a current of chlorine, Na<sub>2</sub>[IrCl<sub>6</sub>] is readily obtained.

Iridium forms the following oxides:

Ir <sub>2</sub> O <sub>3</sub> ,?	IrO <sub>2</sub> ,	and the hydroxide	Ir(OH) <sub>4</sub> .
Bluish black	Needles with a metallic lustre		Indigo-blue powder

The dark color of the chlorides is very characteristic:

IrCl <sub>3</sub> ,*	IrCl <sub>4</sub> ,
Dark green and brown	Black

### REACTIONS IN THE WET WAY.

A solution of Na<sub>2</sub>[IrCl<sub>6</sub>] should be used.

1. **H<sub>2</sub>S** at first decolorizes the solution, owing to the reduction of the tetrachloride to the trichloride, accompanied by the

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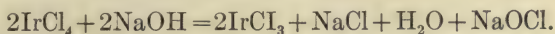
\* According to W. Palmaer, Z. anorg. Chem., **10**, 322-326 (1895), IrCl<sub>3</sub> and its double salts exist in two modifications: dark green and brown.



deposition of sulphur; subsequently brown  $\text{Ir}_2\text{S}_3$  is precipitated, readily soluble in  $(\text{NH}_4)_2\text{S}$ .

2.  $(\text{NH}_4)_2\text{S}$  precipitates the same compound.

3.  $\text{NaOH}$ , on being added to the solution, changes the color from dark red to green; on warming the solution it is at first colored reddish and finally azure blue:



If the solution is now acidified with  $\text{HCl}$ , a little alcohol\* added and then some  $\text{KCl}$ , there will be no precipitation, because the  $\text{K}_3[\text{IrCl}_6]$  formed is readily soluble in water and in  $\text{KCl}$  solution (difference from platinum).

4.  $\text{KCl}$  precipitates brownish-black potassium iridium chloride,  $\text{K}_2[\text{IrCl}_6]$ , insoluble in  $\text{KCl}$  and in alcohol, difficultly soluble in water.

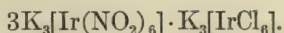
5.  $\text{NH}_4\text{Cl}$  precipitates dark-red ammonium iridium chloride,  $(\text{NH}_4)_2[\text{IrCl}_6]$ , insoluble in a saturated solution of  $\text{NH}_4\text{Cl}$ .

6. **Reducing Agents** usually change the solution to a greenish color, owing to the reduction of the tetrachloride to trichloride; or the solution is decolorized and the black, finely-divided metal is deposited.

Thus if the solution is warmed with  $\text{KNO}_2$ , an olive-green coloration is produced:



If the solution is boiled for some time with an excess of  $\text{KNO}_2$ , it becomes yellow, and a part of the iridium separates out in the form of a yellowish-white precipitate, difficultly soluble in cold hydrochloric acid or in boiling water. The precipitate has the following composition:



Oxalic acid, ferrous sulphate, stannous chloride, and hydroxylamine reduce the tetrachloride to trichloride. Zinc reduces it to metal, and so does formic acid on warming in the presence of

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\* The alcohol reduces  $\text{NaOCl}$  to  $\text{NaCl}$ .

## ANALYSIS OF THE PLATINUM METALS.\*

The six platinum metals, in the presence of gold and mercury, are assumed to be present in solution as chlorides. The solution is placed in a small retort, treated with dilute  $\text{HNO}_3$ , heated to boiling, and the vapors conducted into NaOH solution. The solution remaining in the retort contains the remaining metals.

<p>If the NaOH becomes yellow, Os may be present. In this case, the odor of <math>\text{OsO}_4</math> will be detected on acidifying with HCl; and if a little <math>\text{Na}_2\text{S}_2\text{O}_3</math> is then added and the solution warmed, a brown precipitate of osmium sulphide will be formed showing the presence of Os.</p>	<p>After cooling, a few cubic centimeters of ether are added, the liquid shaken, and the ether layer removed by means of a separatory funnel. The solution is repeatedly shaken with ether until the ether extract appears colorless.</p> <p>ETHEREAL SOLUTION.</p>	<p>If the etheral solution is yellow, Au<math>_2</math>Cl<math>_3</math> is probably present. The ether is evaporated off, the residue dissolved in a little water, and the resulting solution tested with <math>\text{SnCl}_2</math>; the formation of the purple of Cassius shows the presence of Au.</p>	<p>The dried precipitate, is heated in a porcelain boat in a stream of hydrogen, which causes any Hg to be volatilized; it is subsequently condensed on the colder portions of the tube in the form of a gray coating. The remaining metal after becoming cold again are boiled with hot HCl, in order to remove any Sn or other foreign metal which may have been precipitated with this group on the addition of formic acid. The dried residue is then mixed with common salt and heated to dull redness in a moist chlorine stream (the mass must not melt). After cooling, the residue is treated with water† and ammonium chloride added to the solution so long as a precipitate is formed, which is filtered off.</p> <p>PRECIPITATE. <math>[(\text{NH}_4)_2\text{PtCl}_6, (\text{NH}_4)_2\text{IrCl}_6, (\text{NH}_4)_2\text{RuCl}_6]</math>.</p>	<p>The precipitate is dissolved in hot water, hydroxylamine hydrochloride is added, and the solution allowed to cool. <math>\text{NH}_4\text{Cl}</math> is again added, and the precipitate filtered off.</p> <p>PRECIPITATE. SOLUTION <math>(\text{IrCl}_6(\text{NH}_4)_4, \text{RuCl}_6(\text{NH}_4)_3)</math>.</p>	<p><math>(\text{NH}_4)_2\text{PtCl}_6</math>. A yellow precipitate consisting of regular octahedrons shows the presence of Pt.</p>	<p>This is evaporated to dryness, ignited and fused with KOH and <math>\text{KNO}_3</math> in a silver crucible. The melt is dissolved in water and the bluish-black residue filtered off.</p> <p>RESIDUE. SOLUTION. <math>(\text{Ir}(\text{OH})_3)</math>. <math>(\text{K}_2\text{RuO}_4)</math>.</p>	<p>It is mixed with NaCl and heated from a retort, and the vapors received in alcohol that has been acidified with HCl. A yellowish-brown precipitate is dissolved in water and precipitated with <math>\text{NH}_4\text{Cl}</math>. A black precipitate shows the presence of Ir.</p>	<p>These are soluble in hot concentrated <math>\text{H}_2\text{SO}_4</math> with a yellow color. A small portion is mixed with NaCl and heated in a stream of Cl and the product dissolved in water. A rose-colored solution, which is not precipitated by <math>\text{NH}_4\text{Cl}</math> when dilute, shows the presence of Rh.</p>	<p>The solution is evaporated slowly to dryness, with an excess of <math>\text{NH}_4\text{OH}</math>, and the residue allowed to crystallize from a little warm, dilute <math>\text{NH}_4\text{OH}</math> (insoluble, dark flocks are filtered off; they usually consist chiefly of Ru). The Rh crystallizes as chloropurpureo chloride in yellow crystals, which are filtered off.</p> <p>CRYSTALS: <math>\text{Rh}(\text{NH}_3)_5\text{Cl}_3</math> ■ MOTHER LIQUOR.</p> <p>This contains palladium amine chloride, <math>\text{Pd}(\text{NH}_3)_2\text{Cl}_2</math>. It is saturated with conc. HCl, when crystalline <math>\text{Pd}(\text{NH}_3)_2\text{Cl}_2</math> will be precipitated. This is filtered off, dried in a stream of H<math>_2</math>, ignited, and the residue dissolved in conc. <math>\text{HNO}_3</math>. After cautiously evaporating the brown solution and taking up the residue in water, the solution is treated with <math>\text{Hg}(\text{CN})_2</math>. A yellow precipitate shows the presence of Pd.</p>
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Is rejected.

\* Mylius and Dietz, Ber., 1898, 3187. They recommend this method for the qualitative examination only.

† Chromic acid will impart a yellow or blue color and  $\text{FeCl}_3$  a yellow color.

‡ If a residue remains after extracting with water, it is filtered off and the process repeated; if this does not suffice, it is examined for Ir + Ru after fusing with KOH and  $\text{KNO}_3$ .

ammonium acetate. If considerable mineral acid is present, the reduction takes place less readily.

7. **Chlorine.** If chlorine is conducted into a dilute solution of iridium tetrachloride, the latter becomes reddish-violet according to W. Palmaer;\* after some time the red color disappears and the solution turns brown. The same red color has been observed by Foerster † at an iridium anode in sulphuric acid. According to Palmaer, the red color is due to the formation of an iridium compound having a higher valence than four.

#### REACTIONS IN THE DRY WAY.

On being fused with soda, the gray, brittle metal can be obtained by the action of the upper reducing flame. It is insoluble in aqua regia.

#### Separation of the Platinum Metals.

The separation of the platinum metals is one of the most difficult tasks met with in analytical chemistry. If the metals are already in solution, the table on page 512 can be used to advantage. If, however, the metals are present in a more compact form, it is quite difficult to bring them into solution.

In the latter case the metal is handled in as finely-divided condition as possible (filings, etc.) and treated with aqua regia; this serves to dissolve the greater part of the platinum and palladium, as well as small amounts of rhodium and iridium. The residue (osmium, ruthenium, rhodium, iridium, and small amounts of platinum and palladium) is dried, placed in a porcelain crucible and fused for some time with ten times as much zinc (or lead) in a current of illuminating-gas.‡ In this way the platinum metals are alloyed with the zinc. The mass is allowed to cool in the stream of illuminating gas, and is then treated with hydrochloric acid to dis-

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\* Z. anorg. Chem., 10, 358 (1895).

† Z. Electrochem., 10, 715.

‡ The operation can be very conveniently performed in a common clay pipe. The gas is conducted through the stem and ignited at the bowl. In this way the gas continually streams through the molten alloy, keeps it well stirred, and thereby yields a uniform alloy.



solve out the zinc; this leaves the platinum metals behind in a finely-divided state. They are filtered off from the acid solution, dried, introduced into a porcelain boat, placed in a tube made of difficultly fusible glass, and heated to dark redness in a stream of oxygen.

The greater part of the osmium escapes as osmium tetroxide; it is absorbed by the caustic soda solution and tested according to the table. The residue is intimately mixed with sodium chloride and heated in a moist stream of chlorine. The mass is then dissolved in water and examined according to the table.

If lead were used instead of zinc in the above procedure, the alloy should be treated with dilute nitric acid, which dissolves the lead and the greater part of the palladium. The lead is precipitated with the calculated amount of sulphuric acid, and the filtrate is tested for palladium by transforming it into palladosamine chloride, and then into palladium cyanide. The residue from the nitric acid treatment is treated in the same way as when zinc was used.\*

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\* For more detailed directions for separating the platinum metals, consult the work of Sainte-Claire-Deville, Debray, and Stas: "*Procès verbaux du comité internat. des poids et mesures*," 1877-1878 and 1879.

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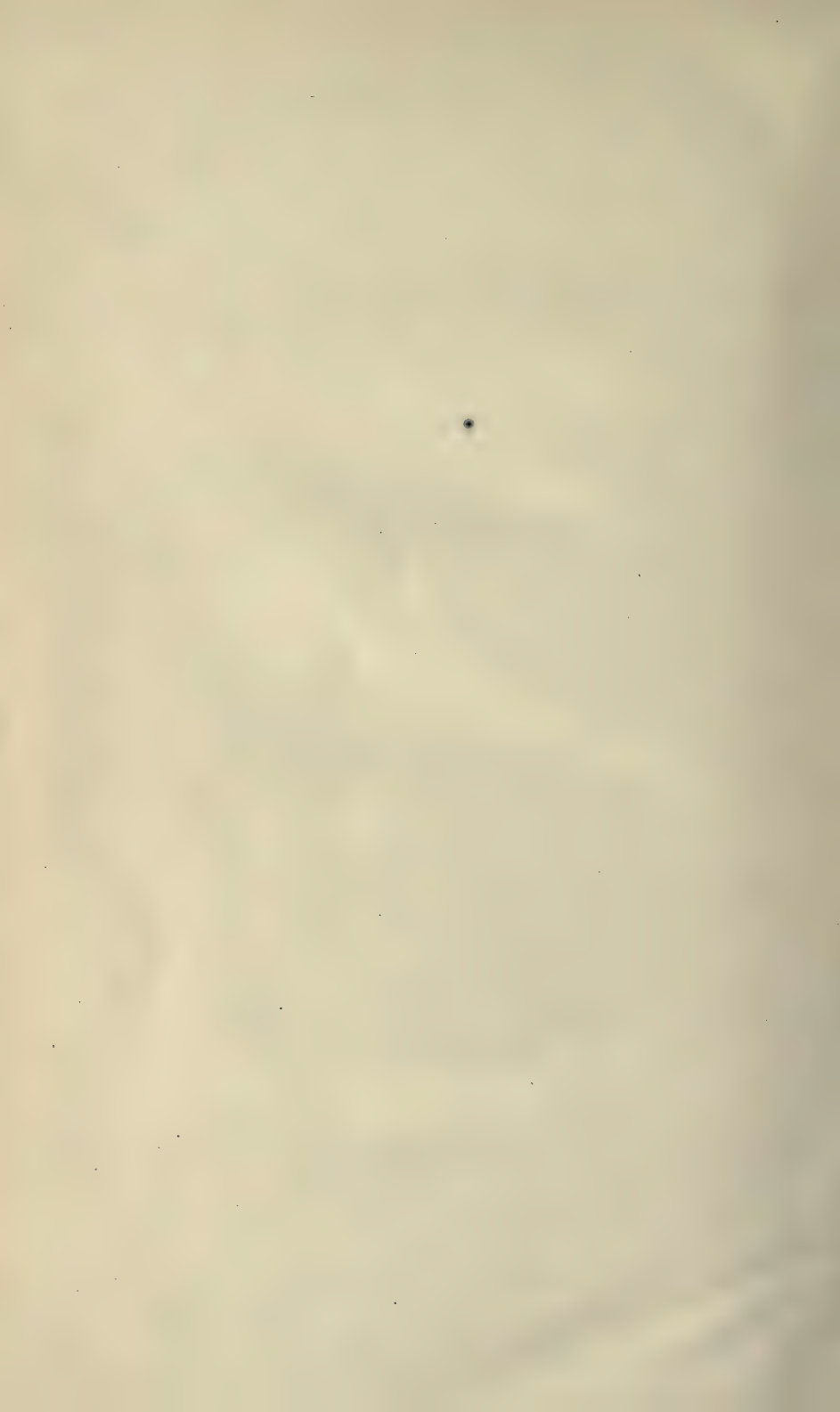
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